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Reviews

New heteroorganic betaines containing the $^{(+)}E^{15}—C—E^{14}—X^{(-)}$ and $^{(+)}E^{15}—C—E^{14(-)}$ structural fragments (E^{15} = P, As; E^{14} = Si, Ge, Sn; X = C, S, O, NR)

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The review surveys the data on the reactions of phosphorus and arsenic ylides with compounds containing E=X bonds (E = C, Si, Ge, or Sn; X = C or S), cyclic oligomers $(R_2ES)_n$ (n = 2 or 3), and heavier analogs of carbenes. These reactions give rise to two new classes of heteroorganic betaines containing the $^{(+)}E^{15}—C—E^{14}—X^{(-)}$ (**I**) and $^{(+)}E^{15}—C—E^{14(-)}$ (**II**) (E^{15} = P or As; E^{14} = Si, Ge, or Sn; X = C or S) structural fragments. Procedures for the synthesis of these compounds, their reactivities, the X-ray diffraction structures, and the electronic structures established by high-level quantum-chemical calculations are considered in detail. The carbon analogs of betaines of type **I**, *viz.*, compounds bearing the $^{(+)}P—C—C—X^{(-)}$ fragment (**III**), are also discussed. The latter were long considered as possible intermediates in the reactions of compounds containing the polar C=X bond (X = C, O, S, NR, *etc.*) with phosphorus ylides (classical Wittig and Corey—Chaykovsky reactions and related processes).

Key words: heteroorganic betaines, phosphorus ylides, silenes, germenes, stannenes, silylenes, germylenes, stannylenes, X-ray diffraction analysis, NMR spectroscopy, density functional theory.

1. Introduction

There are many zwitterionic heteroorganic compounds (betaines) in which the positively and negatively charged centers of different nature are separated by various spacers. Compounds of this type are distinguished by the physical properties and characterized by high and unusual reactivities. Some heteroorganic betaines were surveyed in recent reviews.[1—4] The present review is concerned with new heteroorganic betaines containing the

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$^{(+)}\mathrm{E}^{15}\text{—C—E}^{14}\text{—X}^{(-)}$ (**I**) and $^{(+)}\mathrm{E}^{15}\text{—C—E}^{14(-)}$ (**II**) structural fragments (E^{15} = P or As; E^{14} = Si, Ge, or Sn; X = C, S, O, or NR).

First stable betaines of type **I** in which the phosphonium and arsonium cationic centers are separated from the anionic centers located at the sulfur or carbon atoms by a spacer involving Group 14 elements, *viz.*, silicon, germanium, or tin, have been synthesized and structurally characterized only recently.

$^{(+)}\mathrm{E}^{15}\text{—C—E}^{14}\text{—X}^{(-)}$ **I**

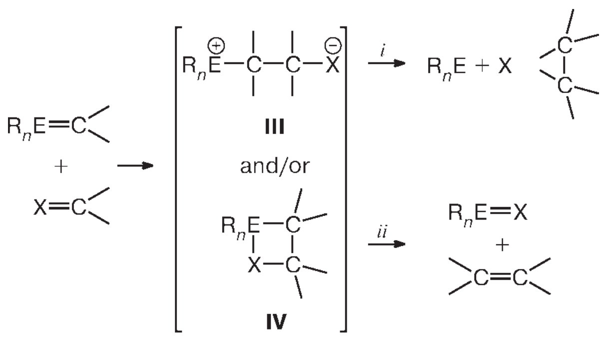
$^{(+)}\mathrm{E}^{15}\text{—C—E}^{14(-)}\text{–}$ **II**

X = C	X = S, O, NR	
$^{+}$P—C—Si—C^{-}	$^{+}$P—C—Si—S^{-}	[$^{+}$P—C—Si^{-}]
$^{+}$P—C—Ge—C^{-}	$^{+}$P—C—Ge—S^{-}	$^{+}$P—C—Sn^{-}
	$^{+}$P—C—Sn—S^{-}	
	$^{+}$As—C—Si—S^{-}	
	$^{+}$As—C—Ge—S^{-}	
	[$^{+}$P—C—Si—O^{-}]	
	[$^{+}$P—C—Si—NR^{-}]	

Betaines of type **I** possessing the anionic centers at the nitrogen and oxygen atoms (these compounds are given in brackets) were observed as intermediates in the reactions of replacement of sulfur in stable thiabetaines of type **I**. Only a small number of betaines of the type $^{(+)}\mathrm{E}^{15}\text{—C—E}^{14(-)}$ (**II**) have been synthesized of which two compounds have been characterized by X-ray diffraction analysis. However, there is a reliable evidence for the intermediate formation of the latter compounds in the reactions of phosphorus and arsenic ylides with silylenes, germylenes, and stannylenes.

Heteroorganic betaines of type **I** can be considered as the closest structural analogs of betaines of the type $^{(+)}\text{P—C—C—X}^{(-)}$ (**III**), which were long believed to be possible intermediates in the classical Wittig and Corey—Chaykovsky reactions and related processes[5,6] (Scheme 1). It was unambiguously proved[7—9] that oxaphosphetanes (**IV**) are the true intermediates in the reactions of "nonstabilized" phosphorus ylides with carbonyl compounds. Betaines $^{(+)}\text{P—C—C—O}^{(-)}$ were detected only as their adducts with lithium salts.[10,11] The fact that thiabetaines $^{(+)}\text{P—C—C—S}^{(-)}$ were formed as the true intermediates in the reactions of phosphorus ylides with thiocarbonyl compounds was first reliably established[12—14] based on the similarity of their spectral characteristics[12] to those of the corresponding thiabetaines $^{(+)}\text{P—C—Si—S}^{(-)}$ **I**, which have been successfully synthesized and completely characterized.[15,16]

Scheme 1



E = P, As, S, *etc.*; X = O, S, Se, NR.

i. Corey—Chaykovsky cyclization;
ii. Wittig olefination.

A comparison of the available data on the reactivities and structures of heteroorganic betaines **I** (X = C or S) and the corresponding carbon analogs $^{(+)}\mathrm{E}^{15}\text{—C—C—X}^{(-)}$ (**III**) revealed their similarity, which opens up new prospects for "variations on the Wittig reaction" in the chemistry of organic derivatives of Group 14 elements, in particular, offers possibilities of the use of betaines **I** as precursors of kinetically unstable compounds containing the E^{14}=X multiple bonds. Upon their generation in solutions, the latter compounds can be involved in further *in situ* transformations. Numerous reactions of carbonyl compounds and alcohols with compounds containing the E^{14}=X bond, which are considered as direct analogs of phosphorus and arsenic ylides, have been already carried out.[17] In recent years, these transformations have attracted growing interest due to the fact that they show considerable promise in practical applications (see, for example, Ref. 18). The present review covers the published data on heteroorganic betaines **I** and **II** up to December 2000 inclusive.

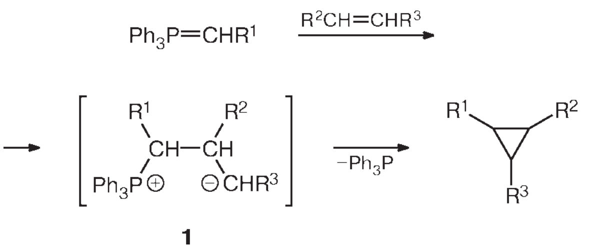
2. Synthesis of heteroorganic betaines $^{(+)}\mathrm{E}^{15}\text{—C—E}^{14}\text{—X}^{(-)}$ (I) and $^{(+)}\mathrm{E}^{15}\text{—C—E}^{14(-)}$ (II) (E^{15} = P, As; E^{14} = Si, Ge, Sn; X = C, S)

Most of the known betaines of both above-mentioned types were prepared by the reactions of phosphorus or arsenic ylides with stable compounds or intermediates containing the E=X bond (E = C, Si, Ge, or Sn; X = C or S), cyclooligomers $(\mathrm{R_2ES})_n$ (n = 2 or 3), three- or four-membered silacarbocycles, or heteroorganic carbene analogs. The reactions of silicon- and germanium-containing organophosphorus thiabetaines with the $(\mathrm{R_3Sn})_2\mathrm{X}$ compounds (X = O or NMe), which proceed through intermediate silicon- or germanium-containing organophosphorus betaines possessing the oxide or alkylamide anionic centers, are considered in Section 5.

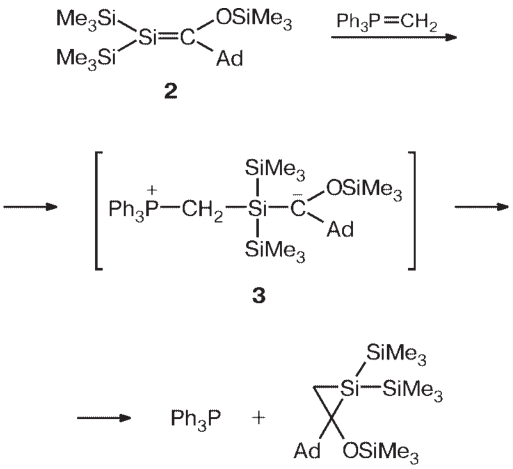
2.1. Synthesis of betaines containing the carbanionic center

It is commonly accepted[5,6,19] that cyclopropanation of olefins containing the polar C=C bond with phosphorus ylides proceeds through unstable betaines **1** (E^{14} = C, X = C) as intermediates (Scheme 2).

Scheme 2



Scheme 3



Ad is 1-adamantyl.

According to the results of the study,[20] the reaction of silaalkene **2** with methylenetriphenylphosphorane (Scheme 3) proceeded analogously.

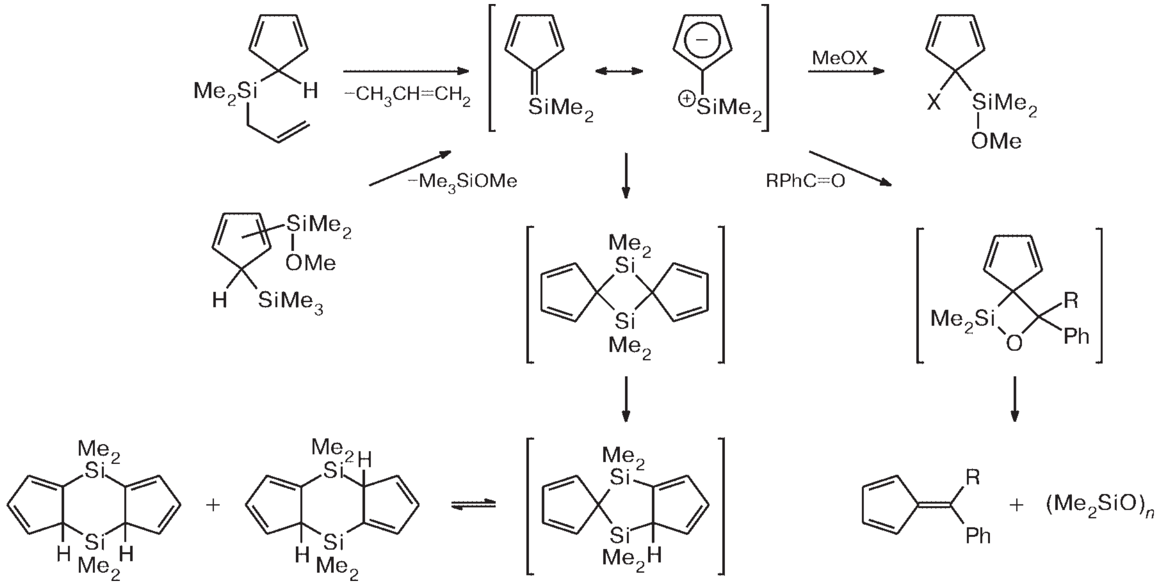
Betaines of types **I** and **III**, such as a series of silafulvenes and dibenzosilafulvenes, were isolated and characterized by multinuclear NMR spectroscopy. The assumption that 6,6-dimethyl-6-silafulvene is more kinetically stable than other silenes was first made by one of the authors of the present review based on analysis of the fragmentation pathways of its molecular ion in the mass spectra and the results of quantum-chemical calculations.[21] This assumption was experimentally confirmed in the studies[22,23] where the formation of 6,6-dimethyl-6-silafulvene was observed in the gas phase (Scheme 4).

6,6-Dialkyl-6-sila-, -germa-, and -stannafulvenes were also generated in solutions by the reactions of phosphorus ylides with cyclopentadienylchlorosilanes, cyclopentadienylchlorogermane, or cyclopentadienylchlorostannane, respectively.[24—30] An alternative pathway of the formation of silafulvene dimers in solutions[31] was rejected based on the results of experiments using chemical traps (Scheme 5).[32]

In solutions, alkylidenetrialkylphosphoranes serve as efficient scavengers of short-lived silafulvenes, germafulvenes, dibenzosilafulvenes, and dibenzogermafulvenes. The former compounds readily react with the latter to form stable betaines **4**—**6** (Scheme 6).[32—34]

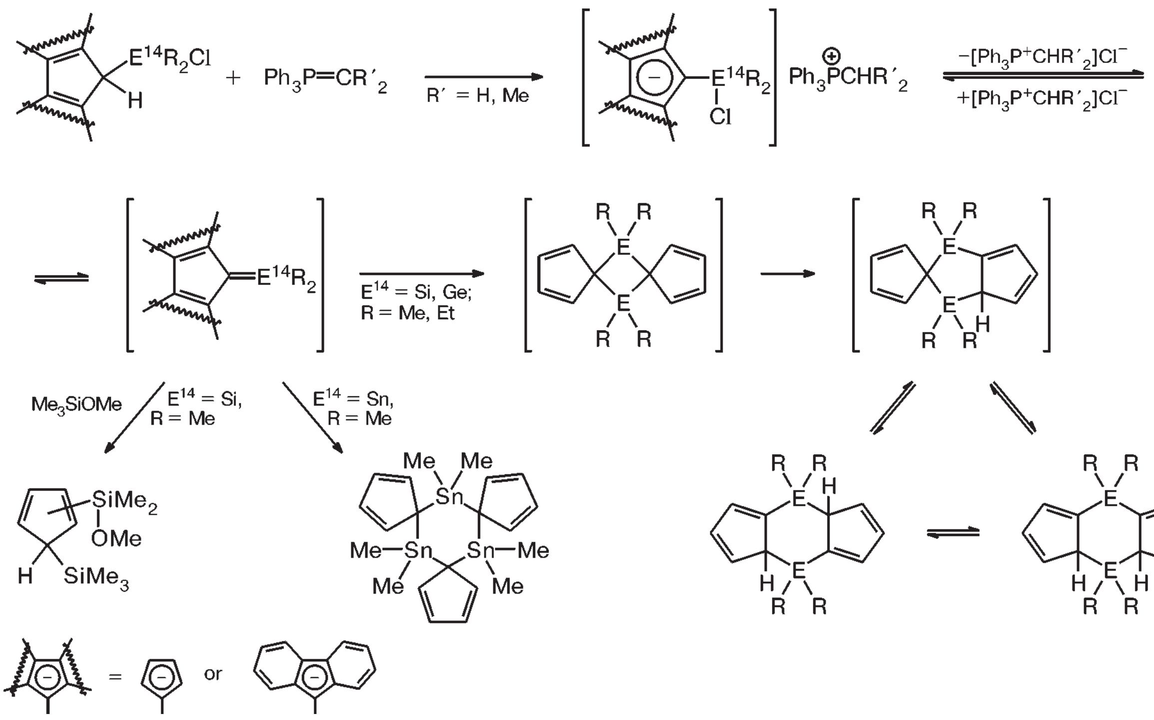
Betaines **4**—**6** are white (for the cyclopentadiene series) or yellow (for the fluorene series) crystalline compounds, which are very sensitive to traces of atmospheric oxygen and moisture. These compounds are poorly soluble

Scheme 4

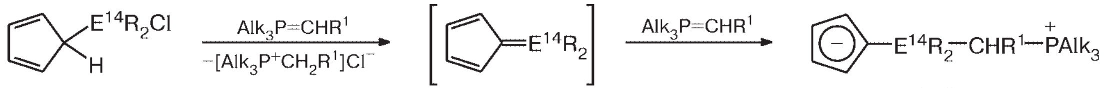


R = H, Ph; X = H, D.

Scheme 5

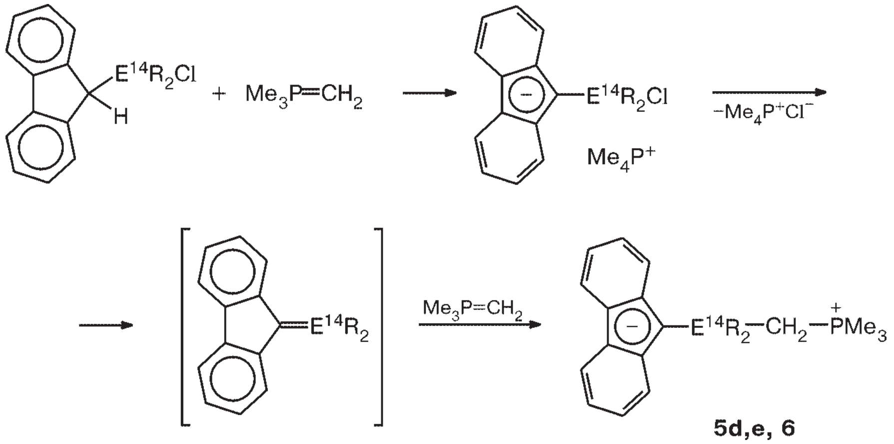


Scheme 6



4, 5a—c

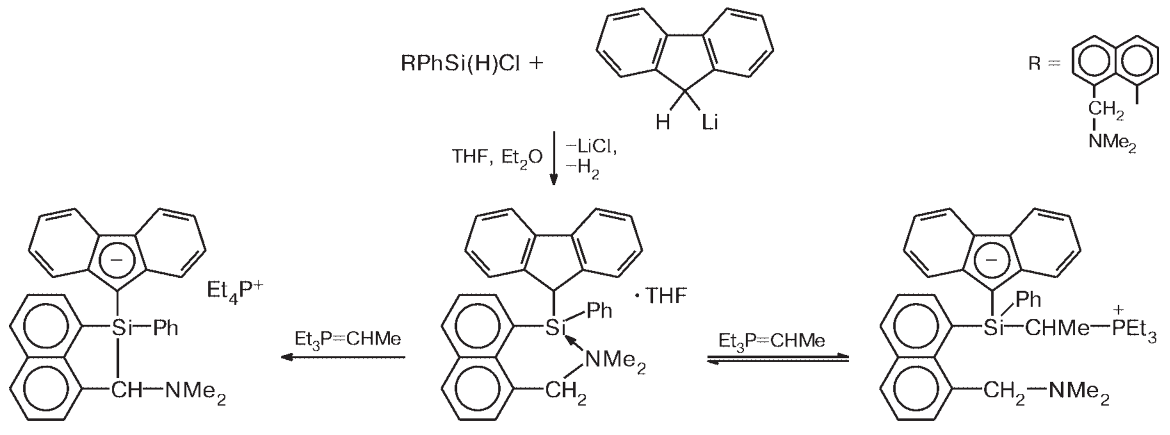
Compound	E^{14}	R	R^1	Alk	Yield (%)
4	C	Me	H	Me	70
5a	Si	Me	H	Me	~100
5b	Si	Me	Me	Et	87
5c	Si	Me$_3$SiCH$_2$	H	Me	91



5d,e, 6

Compound	E^{14}	R	Yield (%)
5d	Si	Me$_3$SiCH$_2$	83
5e	Si	Me, Bu^s	91
6	Ge	Bu^i	87

Scheme 7

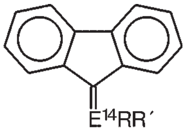


9 **7a** **8**

in low-polarity solvents and are virtually insoluble in nonpolar solvents.

The experimental data on decomposition of these betaines are lacking. However, quantum-chemical calculations demonstrated that the most probable pathway of their decomposition involves elimination of phosphine to form three-membered rings (see Section 6).

The insertion of donor groups, which can be coordinated at the silicon atom, into the dibenzosilafulvene molecule or the insertions of bulky groups into the dibenzogermafulvene and dibenzostannafulvene molecules made it possible to synthesize a series of kinetically stable dibenzosila-, dibenzogerma-, and dibenzostannafulvenes **7** by various methods and then characterize these compounds.[35—43]



7

Compound **7**	E^{14}	R	R′
a	Si	8-Me_2NCH_2Napht	Ph
b	Ge	Mes	Mes
c	Ge	Mes	$(Me_3Si)_2CH$
d	Ge	$(Me_3Si)_2CH$	$(Me_3Si)_2CH$
e	Ge	*cyclo*-Me_5C_5	F
f	Ge	*cyclo*-Me_5C_5	Cl
g	Sn	2,4,6-$Pr^i_3C_6H_2$	2,4,6-$Pr^i_3C_6H_2$

Dibenzosilafulvene **7a** reacted with phosphorus ylide to give betaine **8**, which then underwent the rearrangement into salt **9** under the thermodynamically controlled conditions (Scheme 7).[43]

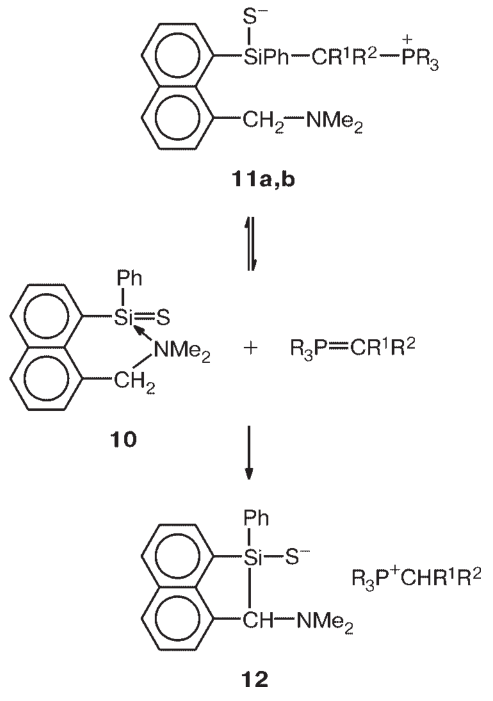
The intermediate formation of betaines containing the carbanionic center was postulated in the reactions of phosphorus ylides with permethylsilirane, silacyclobutane, and disilacyclobutane (see Section 5.1.5).

2.2. Synthesis of betaines containing thiolate centers

2.2.1. Reactions of phosphorus ylides with silanethione 10 and thiocarbonyl compounds

The first silicon-containing organophosphorus betaine possessing the thiolate center (**11a**) was prepared by the reaction of stable silanethione **10** with trimethylmethylenephosphorane (Scheme 8) and characterized by

Scheme 8

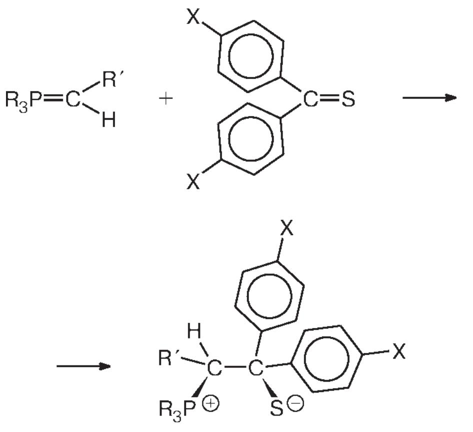


Compound	R	R^1	R^2
11a	Me	H	H
11b	Ph	Me	Me

multinuclear NMR spectroscopy.[15] Under the kinetically controlled conditions, the reaction afforded betaine **11a**. Under the thermodynamically controlled conditions, the latter was transformed into the phosphonium salt of silaacenaphthene **12**. The processes shown in this scheme reflect the competition between the basicity and nucleophilicity of phosphorus ylides. In the reaction mixture, the equilibrium concentration of betaine **11b**, which was prepared from thione **10** under the action of less nucleophilic and less basic ylide containing the phenyl substituents at the phosphorus atom, was no higher than 6%.

Based on the spectral characteristics of betaine **11a** and other silicon-containing organophosphorus betaines (see Section 2.2.2), it was reliably demonstrated that the reactions of phosphorus ylides with thiocarbonyl compounds, unlike the classical Wittig reaction, proceeded through the intermediate formation of betaines **13** [12–14,44] (Scheme 9).

Scheme 9



13a—n

	R_3	R′	X		R_3	R′	X
a	Et_3	Me	Me_2N	**h**	*cyclo*-$PrPh_2$	H	MeO
b	Ph_3	Me	Me_2N	**i**	*cyclo*-Pr_2Ph	H	MeO
c	Ph_3	H	H	**j**	*cyclo*-Pr_3	H	MeO
d	Ph_3	H	MeO	**k**	*cyclo*-Pr_3	H	Me_2N
e	$MePh_2$	H	MeO	**l**	$EtPh_2$	Me	MeO
f	Me_2Ph	H	MeO	**m**	Et_2Ph	Me	MeO
g	Me_3	H	MeO	**n**	Et_3	Me	MeO

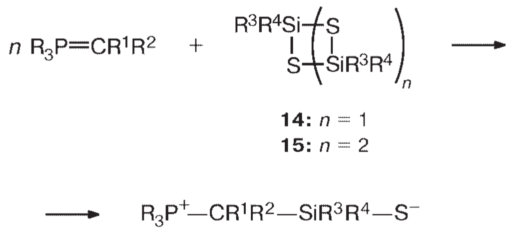
Later on, it was found that the structures of the intermediates of the Wittig reaction in the series of thiocarbonyl compounds depend on the temperature, polarity of the solvent, and other factors. The authors believed[13,14,44] that different compounds, which are structurally intermediate between thiabetaines and thiaphosphetanes, can be generated depending on the reaction conditions and that a continuum of these structures occurs.

Compounds containing the E=S multiple bonds (E = Si, Ge, or Sn), which are stable under standard conditions, are few in number and their generation as intermediates usually requires relatively drastic conditions.[45–49] It was established that the general procedure for the synthesis of heteroelement-containing organophosphorus betaines **I** with the thiolate center involves the reactions of phosphorus or arsenic ylides with organocyclosilathianes, organocyclogermathianes, and organocyclostannathianes.

2.2.2. Synthesis of betaines $^{(+)}E^{15}$—C—E^{14}—$S^{(-)}$ (E^{14} = Si, Ge, Sn) by the reactions of phosphorus and arsenic ylides with silathiacyclanes and their organogermanium and organotin analogs

Disiladithiacyclobutanes **14** and trisilatrithiacyclohexanes **15**, which can formally be considered as dimers and trimers of silanethiones, respectively, readily react with "nonstabilized" phosphorus ylides in various solvents at room temperature to give betaines $R_3P^+—CR^1R^2—SiR^3R^4—S^-$ (**16**) in high yields (Scheme 10).[50,51] Under the same conditions, the cyclotrimer of thioacetone did not react with $Et_3P=CHMe$.

Scheme 10



16a—q

16	R	R^1	R^2	R^3	R^4	**16**	R	R^1	R^2	R^3	R^4
a	Ph	Me	Me	Me	Me	**j**	Ph	Me	Me	Me	OEt
b	Ph	Me	Me	CD_3	CD_3	**k**	Ph	H	Me	Me	Me
c	Ph	CD_3	CD_3	Me	Me	**l**	Ph	H	H	Me	Me
d	Ph	CD_3	CD_3	CD_3	CD_3	**m**	Ph	H	H	Me	Ph
e	Ph	Me	Me	Me	Bz	**n**	Et	H	Me	Me	Me
f	Ph	Me	Me	Me	Ph	**o**	Et	H	Me	Ph	Ph
g	Ph	Me	Me	Ph	Ph	**p**	Me	H	H	Ph	Ph
h	Ph	Me	Me	Ph	H	**q**	Me_2N	Me	Me	Me	Me
i	Ph	Me	Me	Et	H						

The nature of the substituents at the silicon atom has a substantial effect on the course of the reaction. Apparently, the steric effect is of first importance. Thus, a mixture of oligomers $(Me_2SiS)_n$ (n = 2 or 3) reacted with $Ph_3P=CMe_2$ for several hours to give **16a** in 90% yield. The analogous reactions of oligomers $(Ph_2SiS)_n$ afforded **16g** in low yield (25%), whereas oligomers $(Pr^i_2SiS)_n$ did not react at all with phosphorus ylides under analogous conditions.

The nature of ylide is also of importance in these reactions. The higher the nucleophilicity of ylide, the higher the reaction rate and the higher the stability of the resulting betaines in solutions. Trialkylalkylidene- and alkylidenetris(dialkylamino)phosphoranes possess the highest reactivities with respect to oligomers **14** and **15**. The possibility of substantial charge delocalization in the ylide fragment leads to a decrease in the reactivity. Under the above-described conditions, "semistabilized" phosphorus ylides, for example, $Ph_3P{=}CHPh$ did not react with $(Me_2SiS)_n$.[51]

All betaines **16** are white or pale-yellow crystalline compounds, which can be stored under an inert atmosphere over any period, however long, but are highly sensitive to atmospheric oxygen and moisture. These compounds are poorly soluble in benzene and ether, moderately soluble in THF and acetonitrile, and readily soluble in pyridine.

The reactions of dimers **14** and trimers **15** with phosphorus ylides proceeded stepwise. The reaction of $(Me_2SiS)_3$ with $Ph_3P{=}CHMe$ taken in a ratio of 3 : 2 produced betaine **17** (Scheme 11). This compound is stable in the solid state but is reversibly transformed into a mixture of betaine **16k** and $(Me_2SiS)_3$ in a pyridine solution. According to the NMR data, the equilibrium concentration of **16k** at ~20 °C was no higher than 28% and the addition of one more equivalent of $Ph_3P{=}CHMe$ to the reaction solution resulted in the quantitative transformation of **17** into **16k**.

Scheme 11

$$3\ Ph_3P{=}CHMe + 2\ \underset{\mathbf{15}}{(Me_2SiS)_3} \rightleftharpoons$$

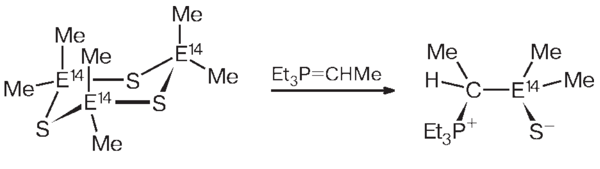
$$\rightleftharpoons 3\ \underset{\mathbf{17}}{Ph_3P^{+}{-}CHMe{-}SiMe_2{-}S{-}SiMe_2{-}S^{-}} \rightleftharpoons$$

$$\rightleftharpoons 3\ \underset{\mathbf{16k}}{Ph_3P^{+}{-}CHMe{-}SiMe_2{-}S^{-}} + (Me_2SiS)_3$$

The reactions of hexamethyltrigermatrithiane **18** and the corresponding tristannatrithiane **19** with $Et_3P{=}CHMe$ afforded the first representatives of organogermanium (**20**) and organotin betaines (**21**) with the thiolate center[52,53] (Scheme 12). These compounds are finely crystalline white compounds, which are similar to their silicon analog **16n** in both the solubility and stability in the solid state and solutions.

The resistance of the E^{14}—S bond in trimetallathianes toward nucleophilic reagents, for example, water or alcohols, is enhanced on going from silicon compounds to germanium and tin derivatives.[54] Apparently, this is responsible for the fact that the reactions of less nucleophilic ylides bearing the phenyl groups at the phosphorus atom with trithianes $(R_2E^{14}S)_3$ (E^{14} = Ge or Sn) proceeded slowly and were complicated by side processes.

Scheme 12



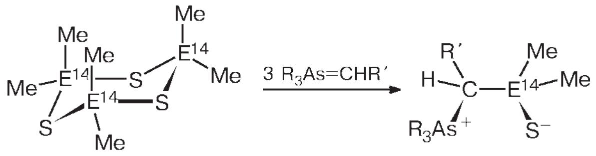
18, 19

20 (84%)
21 (50—90%)

E^{14} = Ge (**18**, **20**); Sn (**19**, **21**)

Since arsenic ylides $R_3As{=}CR^1R^2$ are much more nucleophilic than phosphorus ylides,[55,56] they react substantially more actively with thiacyclanes $(R_2E^{14}S)_n$. Thus, "semistabilized" arsenic ylides $R_3As{=}CHPh$ and $Et_3As{=}CHSiMe_3$ readily reacted with $(Me_2SiS)_n$ and $(Me_2GeS)_3$ (Scheme 13) to form betaines **22** and **23**, respectively, in good yields.[57] Betaines **22a,c** and **23** are stable white crystalline compounds, which are similar in properties and solubility to organophosphorus betaines **16**. Unlike these compounds, betaine **22b** in solution is transformed into disilolane during several hours (see Section 5).

Scheme 13



15, 18

22a—c, 23

E^{14} = Si (**15**, **22**); Ge (**18**, **23**)

Compound	E^{14}	R	R′	Yield (%)
22a	Si	Et	Ph	45
22b	Si	Ph	Ph	~95
22c	Si	Et	Me_3Si	84
23	Ge	Et	Me_3Si	76

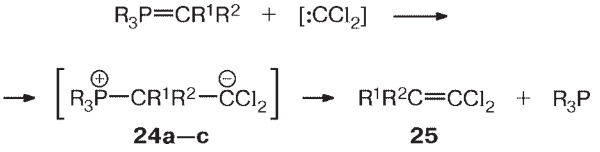
2.3. Synthesis of betaines II

The reactions of dichlorocarbene with phosphorus ylides proceeded, apparently, through intermediate betaine **24** to give dichloroalkenes **25** and phosphines (Scheme 14).[58—60]

First organophosphorus betaines $^{(+)}E^{15}{-}C{-}E^{14(-)}$ (**27**) bearing a negative charge on the atom of a Group 14 element were prepared[61] by the reactions of cyclic stannylene **26** with phosphorus ylides (Scheme 15).

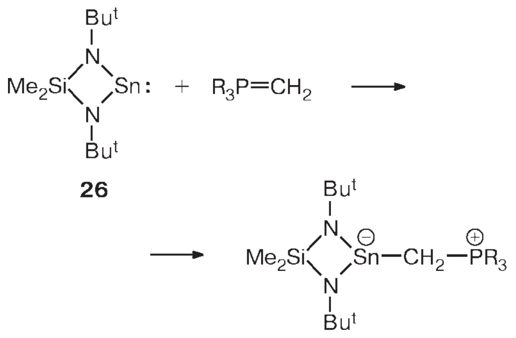
Many of the known stable silylenes, germylenes, and stannylenes, for example, cyclic diaminosilylene **28**,[62] dialkoxygermylene $Ge(OCH_2CH_2NMe_2)_2$ (**29**),[63] and

Scheme 14



Compound	R	R^1	R^2
24a	Bu	H	H
24b	Ph	H	H
24c	Ph	H	Et
25		H	H, Et

Scheme 15

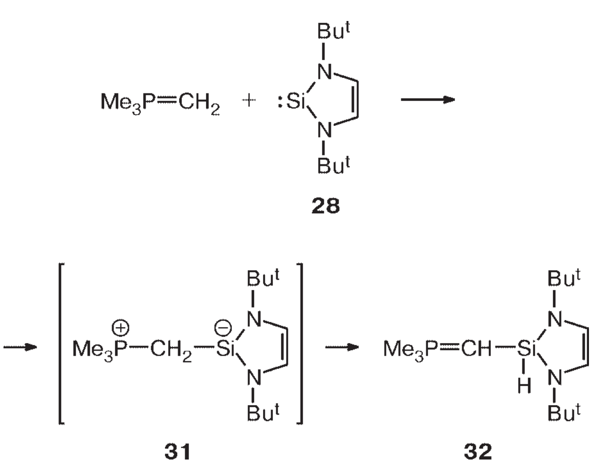


26

27a: R = Me
27b: R = Ph

diphenoxystannylene $Sn[OC_6H_2(CH_2NMe_2\text{-}2,4,6)_3]_2$ (**30**),[64] belong to nucleophilic carbene analogs due to which their reactivities with respect to phosphorus ylides are lowered. However, the reaction of silylene **28** with methylenetrimethylphosphorane produced intermediate betaine **31**, which was isomerized into silylated ylide **32** (Scheme 16).[65] Isomerization of betaines to give the corresponding substituted phosphorus ylides is considered in Section 5.

Scheme 16

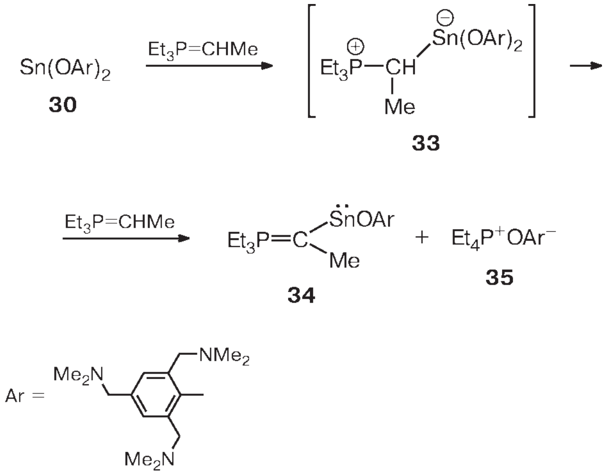


28

31 **32**

According to the NMR data, di(aryloxy)stannylene **30** reacted with ethylidenetriethylphosphorane taken in a ratio of 1 : 2 to form phosphonium salt **35** and new stannylene **34** in which the tin atom is bound to the ylide carbon atom of the starting phosphorane (Scheme 17).[66]

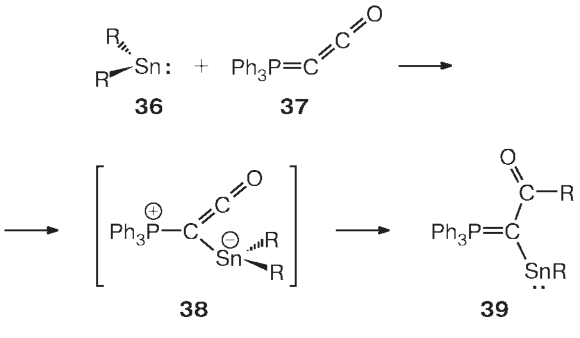
Scheme 17



30 **33** **34** **35**

Structurally similar stannylene (**39**) was prepared by the reaction of phosphorus ylide (**37**) with bis[2,4,6-tris(trifluoromethyl)phenyl]stannylene (**36**), which proceeded, conceivably, through intermediate betaine (**38**) (Scheme 18).[67]

Scheme 18



36 **37** **38** **39**

R = 2,4,6-$(CF_3)_3C_6H_2$

3. Structures of betaines $^{(+)}E^{15}$—C—E^{14}— $S^{(-)}$ (I) and $^{(+)}E^{15}$—C—$E^{14(-)}$ (II) (E^{15} = P, As; E^{14} = C, Si, Ge) according to X-ray data

The principal geometric parameters of betaines **I** are given in Table 1.

Table 1. Principal structural parameters of betaines $^{(+)}E^{15}$—C—E^{14}—S^- (**I**), $^{(+)}E^{15}$—C—$E^{14(-)}$ (**II**), and $^{(+)}$P—C—C—$S^{(-)}$ (**III**) and salt **40** according to the X-ray diffraction data

Compound	E^{15}—C	C—E^{14}	E^{14}—S	E^{15}...S	E^{15}—C—E^{14}	C—E^{14}—S	E^{15}—C—E^{14}—S	Reference
	d/Å				φ/deg			
				P—C—C—S betaines				
13n	1.845(7)	1.554(8)	1.833(6)	3.109(5)	113.0(4)	105.9(4)	47.7(5)	13
13k	1.806(3)	1.557(4)	1.841(3)	3.312(2)	117.6(2)	107.6(2)	52.9(3)	14
				P—C—Si—S betaines				
16a	1.825(4)	1.986(4)	2.048(2)	3.988(4)	115.6(2)	114.6(1)	56.1(2)	16, 68
16a´	1.83(1)	1.98(1)	2.035(5)	3.925(6)	117.9(5)	114.1(4)	46.8(7)	16
16o	1.811(3)	1.934(4)	2.044(2)	3.681(4)	112.8(1)	114.7(2)	38.2(2)	68
16q	1.830(4)	1.979(3)	2.037(2)	3.980(4)	115.7(2)	116.9(1)	50.4(2)	16, 68
				P—C—Ge—S betaines				
20*	1.783(3), 1.785(2)	2.032(3), 2.041(3)	2.140(7) 2.140(7)	3.774(2), 3.810(2)	114.35(13), 114.88(12)	114.86(7), 115.47(7)	25.9(2), 27.3(2)	52
				As—C—Si—S betaines				
22a	1.936(2)	1.946(4)	2.0455(11)	3.518(1)	111.44(17)	109.97(8)	33.13(19)	57
				P—C—Sn betaines				
27b	1.753(8)	2.442(6)	—	—	123.3(3)	—	—	73
27b´	1.74(1)	2.40(1)	—	—	121.9(4)	—	—	61, 73
41	1.710(5)	2.278(5) 2.293(5)	—	—	105.1(2) 119.2(2)	—	—	73
				P,Si,S salt				
40	1.839(5)	1.933(6)	2.140(3)	5.010(5)	116.6(3)	107.3(2)	177.0(2)	16, 68

* For two independent molecules.

In the crystals, the main chain of betaines **I** and their carbon analogs **III** adopts a sterically strained *gauche* conformation (Figs. 1—3) due to strong intramolecular Coulomb interactions between the unlikely charged $^{(+)}E^{15}$ and $S^{(-)}$ centers (see also Section 6). In organophosphorus Si- (**16**)[16,68] and C-betaines (**13**),[13,14,44] the P—C—E^{14}—S dihedral angles are in the range of 38°—56°. For betaines of the carbon series, the P...S nonbonded distances, although being larger than the sum of the covalent radii of the phosphorus and sulfur atoms (2.3 Å), are substantially smaller than the sum of their van der Waals radii (3.65 Å).[69] This leads to considerable steric strains, which are manifested in elongations of all bonds in the main P—C—E^{14}—S chain, particularly, of the central C—E^{14} bonds. Thus, these bond lengths in thiabetaines **13** and **16** are larger than the average values by more than 0.1 Å. The C—Si—S^- and P^+—C—Si bond angles are larger than the ideal tetrahedral value (109.5°) and the phosphorus atoms acquire a distorted tetrahedral configuration.

The insertion of bulkier groups at the silicon atom and, on the contrary, a decrease in steric hindrance at the carbon atom in betaines of the silicon series leads to a decrease in the P—C—Si—S dihedral angle, shortening of the $^+$P...S^- nonbonded contact, and a decrease in the C—Si bond length. A comparison of the geometric

Et_3P^+—CHMe—$C(C_6H_4OMe\text{-}p)_2$—S^-

13n

cyclo-Pr_3P^+—CH_2—$C(C_6H_4NMe_2\text{-}p)_2$—$S^-$

13k

Ph_3P^+—CMe_2—$SiMe_2$—S^-

16a

$[Ph_3P^+$—CMe_2—$SiMe_2$—$S^-] \cdot Ph_3PS \cdot MeOH$

16a´

Et_3P^+—CHMe—$SiPh_2$—S^-

16o

$(Me_2N)_3P^+$—CMe_2—$SiMe_2$—S^-

16q

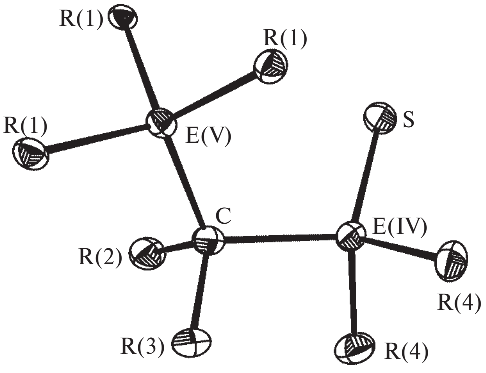


Fig. 1. Overall view of the molecular structure of thiabetaines $^{(+)}E^{15}$—C—E^{14}—$S^{(-)}$ (**13k,n** and **16a,o,q**).

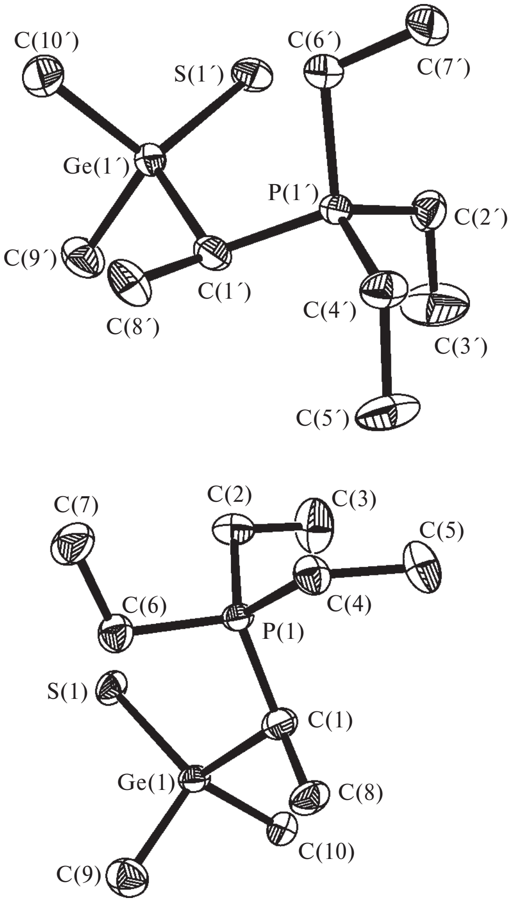


Fig. 2. Crystal structure of thiabetaine $Et_3P^+—CHMe—GeMe_2—S^-$ (**20**) (two independent molecules with thermal ellipsoids drawn at the 50% probability level).

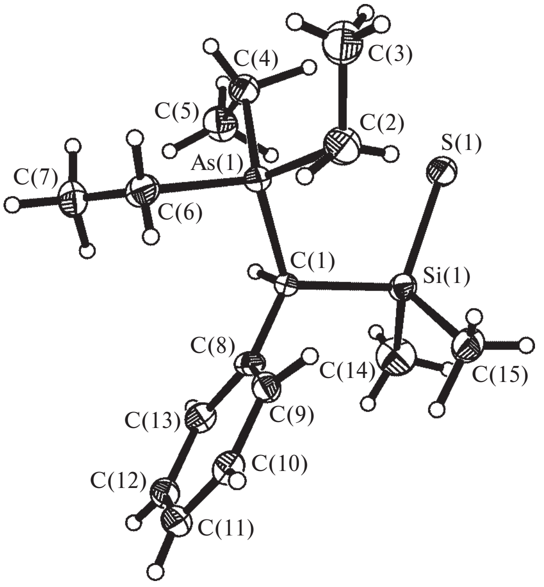


Fig. 3. Crystal structure of thiabetaine $Et_3As^+—CHPh—SiMe_2—S^-$ (**22a**) (with thermal ellipsoids drawn at the 50% probability level).

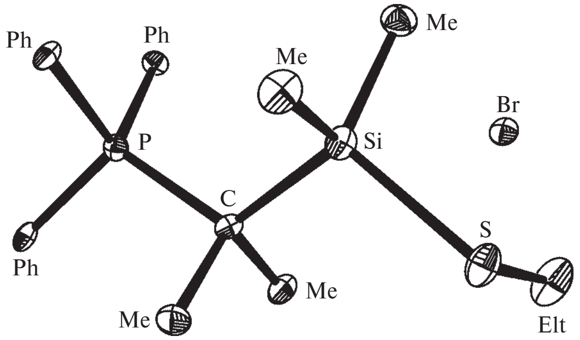


Fig. 4. Crystal structure of the $[Ph_3P^+—CMe_2—SiMe_2—SEt]Br^-$ salt (**40**).

parameters of betaines **16o** and **16a,q** provides clear evidence for the tendency to the closure of the four-membered ring under the influence of these changes.

The $Si—S^{(-)}$ bonds in betaines **16** are shorter than the typical single bonds (2.14 Å)**[70]** but are longer than the Si=S double bonds (1.948(4) Å).**[71]** To the contrary, the $C—S^{(-)}$ bond lengths in their carbon analogs **13** are equal or even somewhat larger than the average C—S single bond length (1.82 Å).**[70]**

Ethylation of betaine **16a** at the sulfur atom afforded salt **40** in which the main chain adopts the sterically most favorable *trans* conformation**[16,68]** (Fig. 4).

$[Ph_3P^+—CMe_2—SiMe_2—SEt]Br^-$

40

On the whole, the geometric structure of organogermanium betaine **20** **[52]** is similar to that of the corresponding silicon analog **16o**. The main differences are an additional shortening of the P—C bond and a further decrease in the torsion angle of the main chain with a simultaneous increase in the $^{(+)}P...S^{(-)}$ distance. Hence, steric strains in molecule **20** are substantially weakened, which is reflected in high thermal stability of this compound (see Section 5).

$Et_3P^+—CHMe—GeMe_2—S^-$

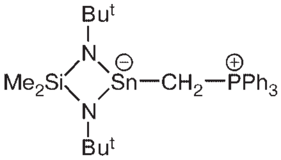
20

In silicon-containing arsonium betaine **22a**,**[57]** the dihedral angle in the main chain is increased compared to that in the above-considered betaine of the germanium series. However, the molecule retains the very short As...S nonbonded contact (3.518(1) Å) whose length is substantially smaller than the sum of the corresponding van der Waals radii (~4.20 Å) although being substantially larger than the As—S single bond lengths (2.20—2.50 Å)**[72]** (see Fig. 3). The nonbonded contact between the hydrogen atom in the *ortho* position of the phenyl ring and the As atom (As(1)...H(9), 3.23(1) Å) is indicative of considerable steric strains in the molecule. The coordination environment about the As atom in this molecule can be considered as either a distorted tetrahedron or a distorted trigonal bipyramid with a substantial deviation of the arsenic atom (0.655 Å) from the C(1)—C(2)—C(6) equatorial plane of the trigonal bipyramid. These structural features of arsonium betaine **22a** are manifested in the fact that this compound readily undergoes selective Corey—Chaykovsky-type decomposition and are reflected in its NMR spectroscopic parameters.

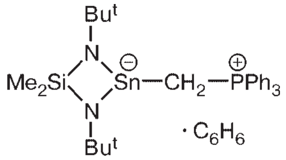
$Et_3As^+—CHPh—SiMe_2—S^-$

22a

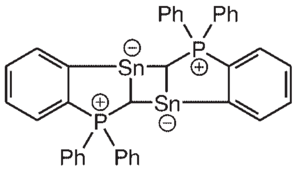
Only three structures of betaines **II** are known, *viz*., **27b**, **27b´**, and **41**. Hence, no general conclusions about their structural features can be made. It can only be noted that the P—C distances in compounds **27b,b´** are shortened as compared to those in betaines **I** and the standard P—C bond length (1.80 Å).[70] In crystal solvate **27b´**, betaine **27b** is present as its conformer. The structures of these compounds differ primarily in that there is a short nonbonded contact between the hydrogen atom in the *ortho* position of one of the Ph rings at the phosphorus atom and the nitrogen atom in the four-membered heterocycle, which was considered[73] as a bridging C—H...N hydrogen bond.



27b



27b´



41

In polycyclic dibetaine **41** generated from **27b´** upon thermolysis (see Section 5), two five-membered rings are perpendicular to the central four-membered ring due to the orthogonal arrangement of the ligands, which is typical of the tin atoms adopting a trigonal-pyramidal configuration.[73] By the type of the bonds with the tin atom, this betaine can be considered as triorganostannate. It should be noted once again that this compound contains the unusually short P—C bond whose length is 0.04 Å smaller than that in betaine **27b** and only 0.05 Å larger than that in $Ph_3P=CH_2$.

According to the X-ray diffraction data, betaines **I** and **II** have characteristic structural features two of which are particularly pronounced in betaines **I**. First, the main chain in these compounds adopts a sterically strained *gauche* conformation due to the intramolecular Coulomb interaction between the cationic and anionic centers and, second, the bond lengths in the main chain are noticeably distorted. The relationship between the structural features of betaines and their reactivities are considered in Section 5.

4. NMR spectroscopic parameters of betaines
$^{(+)}E^{15}$—C—E^{14}—$S^{(-)}$ (I) and $^{(+)}E^{15}$—C—$E^{14(-)}$ (II)
(E^{15} = P, As; E^{14} = Si, Ge, Sn)

Multinuclear NMR spectroscopy is an informative and reliable method for identifying and studying betaines of types **I** and **II** in solutions. The principal NMR spectroscopic characteristics of these compounds are listed in Table 2. The data on some their carbon analogs, *viz*., **4—6** and **13**, are given for comparison.

The characteristics of organophosphorus betaines **4—6**, **12**, **13**, **16**, **17**, **20**, **21**, and **27** are very similar to those of the corresponding phosphonium cations $R_3P^+—CHR^1R^2$ and the cations of silylated phosphonium salts $R_3P^+—CHR^1—SiR^2{}_3$.[74—76] The ^{31}P NMR signals of betaines are observed in the region typical of the tetracoordinated phosphorus atom[77,78] (δ 0—84), whereas these signals in the spectra of intermediate[13] thiaphosphetane and stable thiaphosphetene[79] are observed in the region typical of the pentacoordinated phosphorus atom (δ ~ −40).

The NMR spectra of all phosphorus-containing betaines are characterized by the downfield shift of the ^{13}C signal of the $^{(+)}P—C—E^{14}—S^{(-)}$ main chain with respect to the signals of the corresponding phosphonium cation and the starting phosphorus ylide. This shift is particularly large for C-betaines **13** (by 37—43 ppm relative to the phosphonium cations and by 56—72 ppm relative to ylides) and is substantially smaller for heteroorganic thia- and carbabetaines **5**, **6**, **12**, **16**, **17**, **20**, **21**, and **27**. All direct spin-spin coupling constants $^1J_{PC}$ for C-thiabetaines **13** are much larger (65—82 Hz) than those for the corresponding phosphonium cations $R_3P^+—CHR^1R^2$ (49—61 Hz)[14] but are somewhat smaller than those for the starting ylides $R_3P=CHR^1R^2$ (96—117 Hz).[44,77,78] To the contrary, the constants $^1J_{PC}$ in the spectra of Si-, Ge-, and Sn-betaines of the thiolate[51—53] and carbanionic series[33,34,80] are decreased by 10—26 Hz compared to the corresponding constants in the spectra of the phosphonium cations $R_3P^+—CHR^1R^2$.[77]

The geminal spin-spin coupling constants $^2J_{PH}$ for Si-betaines **5** and **16** and the silylated phosphonium cations[81] are ~4—6 Hz larger, whereas those for C-betaines **4** and **13** are smaller than these constants in the spectra of the corresponding nonsubstituted phosphonium cations.

Polarity of the solvent and the presence of lithium salts have no substantial effect on the spectral character-

Table 2. Selected NMR spectral parameters (δ, J/Hz) of betaines $^{(+)}E^{15}—C—E^{14}—X^{(-)}$ (**I**), $^{(+)}E^{15}—C—E^{14(-)}$ (**II**), and $^{(+)}P—C—C—S^{(-)}$ (**III**)

Betaine	δ_H ($P^+—CH_n$) ($^2J_{PH}$; $^3J_{HH}$)	δ_C ($E^{15(+)}CE^{14}$) ($^1J_{CP}$)	δ_P	δ_{Si} ($^2J_{SiP}$) or $\delta_{PC\underline{C}(Ar)}$ ($^2J_{CP}$)	Reference
$^+P—C—C—C^-$					
$Me_3P^+CH_2CMe_2C_5H_4^-$ (**4**)	2.16 d (12.5)	—	—	—	32
$^+P—C—E^{14}—C^-$					
$Me_3P^+CH_2SiMe_2C_5H_4^-$ (**5a**)	1.21 d (17.8)	—	—	—	32
$Me_3P^+CH_2Si(CH_2SiMe_3)_2C_5H_4^-$ (**5c**)	1.16 d (17.8)	—	—	—	32
$Me_3P^+CH_2Si(CH_2SiMe_3)_2C_{13}H_9^-$ (**5d**)	—	13.35 d (45.1)	22.1	−13.11 d (5.0), 0.03 d (1.1)	33, 34
$Me_3P^+CH_2SiMe(Bu^s)C_{13}H_9^-$ (**5e**)	—	9.68 d (46.4)	21.8	−10.6 d (5.3)	33, 34
$Me_3P^+CH_2Ge(Bu^i)_2C_{13}H_9^-$ (**6**)	—	8.26 d (44.4)	—	—	80
$^+P—C—C—S^-$					
$Et_3P^+CHMeC(C_6H_4$-p-$NMe_2)_2S^-$ (**13a**)	2.20 dq (7.7; 12.3)	49.0 d (67.6)			12, 51
$Ph_3P^+CHMeC(C_6H_4$-p-$NMe_2)_2S^-$ (**13b**)	2.26 br.m (masked)	—	27.33	—	12, 51
$Ph_3P^+CH_2CPh_2S^-$ (**13c**)	—	52 d (82)	5		13, 14
$Ph_3P^+CH_2C(C_6H_4$-p-$OMe)_2S^-$ (**13d**)	5.18 d (9.8)	51.8 d (82.1)	0.4		14
$MePh_2P^+CH_2C(C_6H_4$-p-$OMe)_2S^-$ (**13e**)	5.01 d (10.0)	51.6 d (78.8)	1.9	51.9 d (2.5)	14
$Me_2PhP^+CH_2C(C_6H_4$-p-$OMe)_2S^-$ (**13f**)	4.37 d (10.6)	50.9 d (73.9)	9.2	52.2 d (2.7)	14
$Me_3P^+CH_2C(C_6H_4$-p-$OMe)_2S^-$ (**13g**)	4.05 d (10.5)	49.1 d (75.1)	11.5	51.9 d (3.3)	14
c-$PrPh_2P^+CH_2C(C_6H_4$-p-$OMe)_2S^-$ (**13h**)	5.16 d (10.0)	52.1 d (77.9)	13.9	51.9 d (2.1)	14
c-$Pr_2PhP^+CH_2C(C_6H_4$-p-$OMe)_2S^-$ (**13i**)	4.59 d (9.9)	48.8 d (81.2)	16.8	51.9 d (2.2)	14
c-$Pr_3P^+CH_2C(C_6H_4$-p-$OMe)_2S^-$ (**13j**)	3.89 d (10.6)	46.0 d (71.7)	29.9	51.1 d (1.9)	14
c-$Pr_3P^+CH_2C(C_6H_4$-p-$NMe_2)_2S^-$ (**13k**)	3.89 d (10.2)	46.4 d (72.2)	27.7	50.8 d (1.8)	14
$EtPh_2P^+CHMeC(C_6H_4$-p-$OMe)_2S^-$ (**13l**)	5.50 q (0; 6.6)	57.4 d (70.1)	14.4	58.3 s (0)	14
$Et_2PhP^+CHMeC(C_6H_4$-p-$OMe)_2S^-$ (**13m**)	4.83 q (0; 6.7)	53.8 d (67.4)	25.3	58.2 s (0)	14
$Et_3P^+CHMeC(C_6H_4$-p-$OMe)_2S^-$ (**13n**)	4.65 dq (2.4; 6.8)	48.5 d (67.7)	27.5	57.6 s (0)	14
$^+P—C—Si—S^-$					
$Me_3P^+CH_2SiPhNft$-S^- (**12a**)	—	18.1 d (45.5)	26.5	−7.1 s (2.0)	15
$Ph_3P^+CMe_2SiMe_2S^-$ (**16a**) or $(Ph_3P^+CMe_2SiMe_2S^-)_2 \cdot LiBr$	—	27.7 d (22.9)	39.7	13.8 d (2.2)	51
$Ph_3P^+CMe_2SiMeBzS^-$ (**16e**)	—	28.7 d(23.2)	38.8	13.6 d (1.5)	51
$Ph_3P^+CMe_2SiMePhS^-$ (**16f**)	—	28.9 d (21.7)	40.4	8.0 d (2.9)	51
$Ph_3P^+CMe_2SiPh_2S^-$ (**16g**)	—	30.9 d (23.3)	40.4	1.3 d (3.6)	51
$Ph_3P^+CMe_2SiPh(H)S^-$ (**16h**)	—	25.2 d (22.9)	39.8	—	51
$Ph_3P^+CMe_2SiEt(H)S^-$ (**16i**)	—	24.7 d (23.8)	39.2	9.5 d (1.3)	51
$Ph_3P^+CMe_2SiMe(OEt)S^-$ (**16j**)	—	26.7 d (20.7)	40.1	—	51
$Ph_3P^+CHMeSiMe_2S^-$ (**16k**)	3.17 dq (18.3; 7.2)	17.8 d (32.1)	32.9	6.7 d (2.4)	51
$Ph_3P^+CH_2SiMe_2S^-$ (**16l**)	2.90 d (17.9)	15.2 d (38.1)	26.7	0.2 d (6.3)	51
$Ph_3P^+CH_2SiMePhS^-$ (**16m**)	δ_A 2.85, δ_M 2.72 ($J_{AX} = J_{MX} = 17.5$) ($J_{AM} = 14.5$)	15.1 d (39.5)	26.5	−4.3 d (5.6)	51
$Et_3P^+CHMeSiMe_2S^-$ (**16n**)	1.54 dq (18.1; 7,5)	14.9 d (35.9)	43.7	4.4 d (2.2)	51
$Et_3P^+CHMeSiPh_2S^-$ (**16o**)	2.32—2.51 м^b	13.4 d (35.1)	44.7	−3.2 d (1.0)	51
$Me_3P^+CH_2SiPh_2S^-$ (**16p**)	2.09 d (17.6)	14.2 d (45.5)	26.1	−9.6 d (4.4)	51
$(Me_2N)_3P^+CMe_2SiMe_2S^-$ (**16q**)	—	30.2 d (83.9)	74.1	14.1 d (1.8)	51
$Ph_3P^+CHMeSiMe_2SSiMe_2S^-$ (**17**)	~3.10 (overlapping of signals)	15.9 d (23.4)	31.7	16.1 (SSiS) 17.2 br (PCSi) ($\nu_{1/2}$ = 5.35 Hz)	51
$^+P—C—Ge—S^-$					
$Et_3P^+CHMeGeMe_2S^-$ (**20**)	1.56 dq (15.6; 7.6)	14.1 d (38.2)	43.5	—	52
$^+P—C—Sn—S^-$					
$Et_3P^+CHMeSnMe_2S^-$ (**21**)	br	7.89 d (37.0)	43.6	—	53

(*to be continued*)

Table 2 (*continued*)

Betaine	δ_H (P^+—CH_n) ($^2J_{PH}$; $^3J_{HH}$)	δ_C ($E^{15(+)}CE^{14}$) ($^1J_{CP}$)	δ_P	δ_{Si} ($^2J_{SiP}$) or $\delta_{PC\underline{C}(Ar)}$ ($^2J_{CP}$)	Reference
		$^+$*As—C—Si—S*$^-$			
$Et_3As^+CH(Ph)SiMe_2S^-$ (**22a**)	3.69 s	39.52	—	—	57
$Et_3As^+CH(SiMe_3)SiMe_2S^-$ (**22c**)	1.41 s	15.93	—	0.24 ($SiMe_2$); 1.88 ($SiMe_3$)	57
		$^+$*As—C—Ge—S*$^-$			
$Et_3As^+CH(SiMe_3)GeMe_2S^-$ (**23**)	1.37 s	14.75	—	—	57
		$^+$*P—C—Sn*$^-$			
$Me_3P^+CH_2Sn$—$N(Bu^t)$—$SiMe_2$—$N(Bu^t)$ (**27a**)	0.3 d (12)	—	18	—	61
$Ph_3P^+CH_2Sn$—$N(Bu^t)$—$SiMe_2$—$N(Bu^t)$ (**27b**)	1.62 d (10)	—	24	—	61

istics of Si-thiabetaines **16** in solutions.[51] According to the ^{13}C and ^{31}P CP MAS NMR spectra, these compounds have identical structures both in the crystals and solutions.[51] In contrast, the spectroscopic parameters of C-thiabetaines **13** depend substantially on the nature of the solvent.[14,44] The structures of betaines **13** in low-polarity solvents and in the crystal state are identical.[14]

Phosphorus-containing thiabetaine **20** (E^{14} = Ge)[52] and its analog **21** (E^{14} = Sn)[53] are similar in the spectroscopic characteristics to silicon-containing thiabetaines **16**.

In the ^{13}C and ^{1}H NMR spectra of arsonium Si-containing betaine **22a** at ~20 °C, the resonance signals for C_o and C_m and for H_o, respectively, are broadened, which is, apparently, indicative of hindered rotation about the C—Ph bond.[57] The presence of the chiral carbon atom in the molecule is responsible for diastereotopic doubling of the signals of the methyl groups at the silicon atom. A similar situation is observed in the case of phosphorus-containing analogs. The presence of the chiral E^{14} atom leads to doubling of the signals of the substituents at the α-carbon atom of the E^{15}—C—E^{14} fragment in betaines of type **I**.

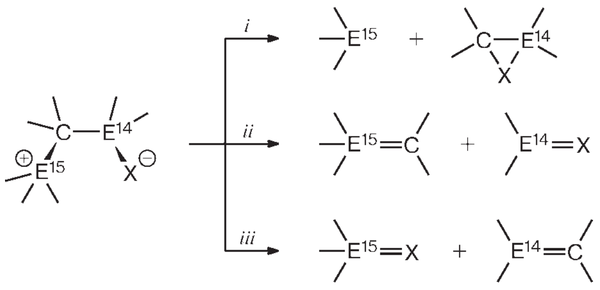
5. Reactivities of betaines $^{(+)}E^{15}$—C—E^{14}—$X^{(-)}$ (I) and $^{(+)}E^{15}$—C—$E^{14(-)}$ (II) (E^{15} = P, As; E^{14} = Si, Ge, Sn; X = S)

Betaines of types **I** and **II** contain several reaction centers due to which they exhibit potentially rich and versatile reactivities. Silicon-containing organophosphorus betaines **I** bearing the thiolate center have received the most study.

5.1. Photodecomposition and thermal decomposition of betaines I and II

The similarity of the structures of betaines **I**, *viz.*, compounds **16**, and their carbon analogs **13** (see Section 3) is clearly manifested in their identical ability to undergo decomposition with the cleavage of the P—C bond in the $^{(+)}$P—C—E—$S^{(-)}$ main chain and elimination of R_3P (Corey—Chaykovsky-type reaction) (Scheme 19).

Scheme 19



E^{14} = Si, Ge, Sn; E^{15} = P, As.

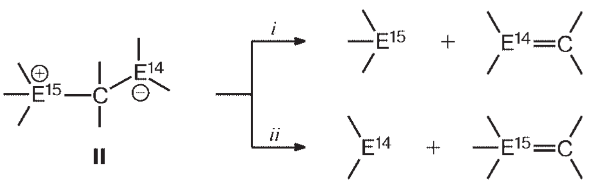
i. Corey—Chaykovsky-type fragmentation;
ii. retro-Wittig-type fragmentation;
iii. Wittig-type fragmentation.

At the same time, further transformations of sterically nonhindered highly reactive thiiranes and silathiiranes differ substantially. According to the results of the studies,[13,44,82] the reactions of the resulting thiiranes and phosphines produce olefins and R_3PS, whereas their silicon analogs, *viz.*, silathiiranes, undergo dimerization in the absence of chemical scavengers.

The second main pathway of decomposition of betaines **16** involves the cleavage of the central C—Si bond by the retro-Wittig-type reaction with elimination of the starting phosphorus ylide and formation of kinetically unstable silanethiones, which undergo further transformations. Betaines **13** can, in principle, undergo this type of decomposition, which is characteristic of the reactions of phosphorus ylides with compounds containing the polar C=X bond.[83] However, this process has not been experimentally observed. Apparently, Wittig-type decomposition is untypical of thiabetaines **16**.

According to the data of quantum-chemical calculations (see Section 6), betaines of type **II** can be decomposed either with elimination of phosphine (path (*i*)) or with the formation of ylide and a heavy analog of carbene (*ii*), the latter process being the reverse of their formation (Scheme 20). The path (*i*) giving rise to the compounds with E^{14}=C double bonds is of much greater interest.

Scheme 20



E^{14} = Si, Ge, Sn; E^{15} = P, As.

5.1.1. Photodecomposition of betaines $^{(+)}E^{15}$—C—Si—$S^{(-)}$ I (E^{15} = P, As)

UV radiation induces the intramolecular $S^- \to P^+$ or $S^- \to As^+$ charge transfer resulting in the cleavage of the E^{15}—C bond and decomposition of betaines $^{(+)}E^{15}$—C—Si—$S^{(-)}$ (**I**) (E^{15} = P or As) according to the Corey—Chaykovsky-type reaction. Thus, betaine **16a** was decomposed to form triphenylphosphine and silathiirane **42a** upon irradiation of its suspension in benzene at 20 °C with the use of a medium-pressure mercury lamp[84] (Scheme 21).

Like other sterically nonhindered heterothiiranes of Group 14 elements,[85—88] silathiirane **42a** is kinetically unstable and is transformed into cyclodimer **43a**. Photolysis of betaine **16a** in an alcoholic solution afforded silylated thiol **44a**. In the presence of acetone, the reaction gave rise also to 1,2,4-oxadithiolane **45a**, which is a product of trapping of silathiirane **42a** by acetone, along with dimer **43a**, the latter still being the major reaction product. Under homogeneous conditions, the starting betaine can also trap silathiirane **42a** (provided that its concentration in the reaction solution is high) to form 1 : 1 adduct **46a**, which then eliminates $Ph_3P=CMe_2$ to produce 1,3,2,4-dithiadisilolane **47a**. Under heterogeneous conditions (suspension in benzene), compound **47a** was obtained in substantially lower yield.

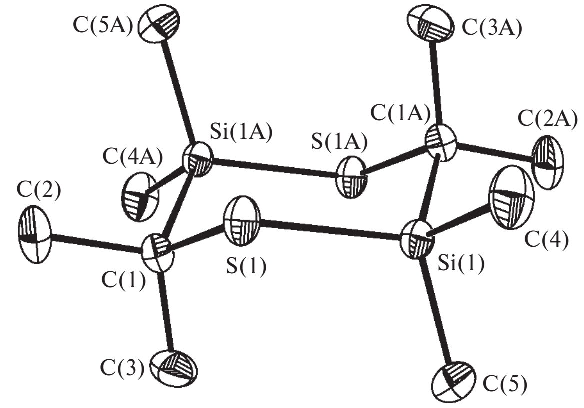
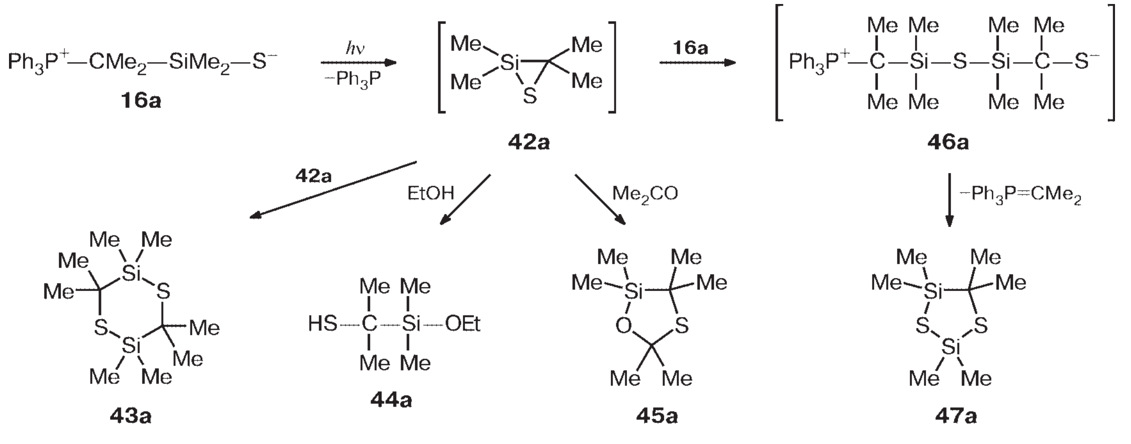


Fig. 5. Structure of compound **43a**.

The structure of cyclodimer **43a** was established by X-ray diffraction analysis (Fig. 5).

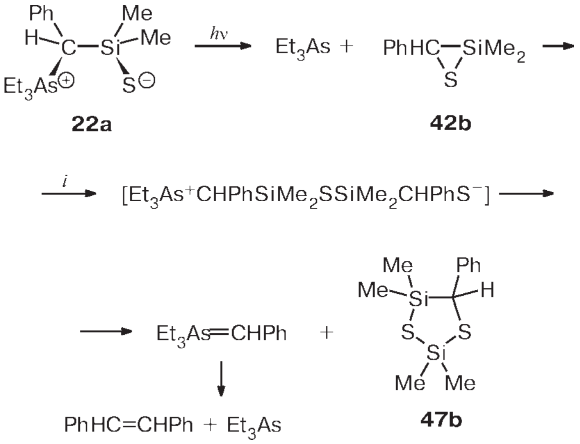
The distinguishing structural feature of compound **43a** is the *trans* effect resulting in distortion of the tetrahedral coordination of the carbon atoms. This effect has been discovered previously in peroxides and ethers.[89] In molecule **43a**, the C(4)—Si(1)—S(1) and C(2)—C(1)—S(1) bond angles in the *trans* positions with respect to the corresponding opposite bonds involving the S atoms are decreased to 102.35(4)° and 104.64(6)°, respectively, as compared to the ideal tetrahedral value (109.5°). The ring adopts a virtually ideal chair conformation (the torsion angles are in the range of 60.4—61.7°).

Scheme 21



Under homogeneous conditions, photodecomposition of arsenic-containing organosilicon thiobetaine **22a** proceeded with high selectivity to give Et_3As and dithiadisilolane **47b** as the only products (Scheme 22).[57]

Scheme 22



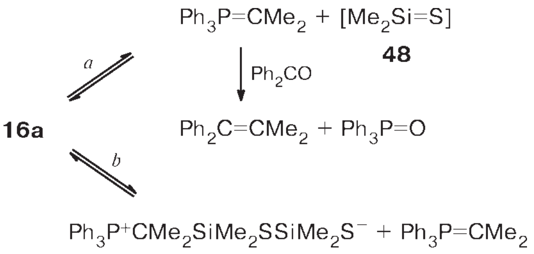
i. Et_3As^+—$CHPhSiMe_2S^-$.

The data on thermal decomposition of phenyl analog **22b** are considered in the following section.

5.1.2. Thermal decomposition of betaines $^{(+)}E^{15}$—C—Si—$S^{(-)}$ (I) (E^{15} = P, As)

Organosilicon thiabetaines containing alkyl or dialkylamino groups at the phosphorus atom are rather resistant toward thermolysis. Thus, betaines **16n—q** remained unchanged upon heating in pyridine solutions to 150 °C under anaerobic conditions for several hours.[84] Betaines containing the phenyl substituents at the phosphorus atom are less thermally stable. Heating of solutions of compound **16a** in C_5D_5N above 80 °C was accompanied by the appearance of the characteristic color of phosphorus ylide and the ^1H, ^{13}C, and ^{31}P NMR spectra of the resulting solutions showed signals of $Ph_3P=CMe_2$ and cyclosilathianes. The fact that decomposition of **16a** proceeded as the retro-Wittig-type reaction (Scheme 23, *a*) was confirmed by the formation of 1,1-dimethyl-2,2-diphenylethylene upon heating (100 °C) of a solution of this betaine in pyridine-d_5 in the presence of benzophenone. Phosphorus ylide can also be formed in the bimolecular equilibrium reaction (see Scheme 23, *b*). The ratio between the contributions of these two processes depends to a large extent on the solvent and temperature.

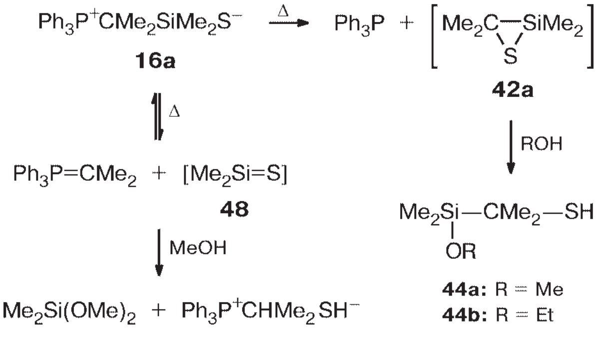
Scheme 23



Both equilibria are shifted to the right as the temperature is increased. After heating (90 °C, ~30 min) of a solution of betaine **16a** in C_5D_5N, the [**16a**] : [$Ph_3P=CMe_2$] concentration ratio (according to the NMR data) was 0.8 : 1. All signals of phosphorus ylide were broadened. This ratio was increased to 2.9 : 1 as the temperature was lowered to 50 °C and then decreased to 1.46 : 1 upon subsequent repeated heating to 75 °C. These ratios cannot be considered as those corresponding to the equilibrium because a series of irreversible processes (see below) occurred in solutions simultaneously with the retro-Wittig-type decomposition.

The selectivity of thermolysis of betaines **16** was lower than that of their photolysis[84] and the former process followed two competitive paths (*i*) and (*ii*) (see Scheme 19), *viz.*, the Corey—Chaykovsky-type and retro-Wittig-type reactions, respectively. The ratio between the contributions of these processes under different conditions can be judged from the composition of the thermolysis products in ethanol. Upon heating of an ethanolic solution of **16a** in a sealed tube, highly reactive silanethione $Me_2Si=S$ (**48**) and silathiirane **42a** that formed immediately reacted with ethanol to produce $Me_2Si(OEt)_2$ and silylated thiol $Me_2Si(OEt)CMe_2SH$ (**44b**), respectively (Scheme 24). At 150 °C, these products were obtained in a ratio of 1 : 1. The Corey—Chaykovsky reaction became the major process at 245 °C. At this temperature, the ratio of $Me_2Si(OEt)_2$ to **44b** was 1 : 3.

Scheme 24



In the case of pyrolysis (150 °C) of thiabetaines **16a,e,f,k** containing the Ph_3P^+ group in C_6H_6, C_5D_5N, or in melts, silathiiranes **42** that formed by the Corey—Chaykovsky-type reaction were subsequently

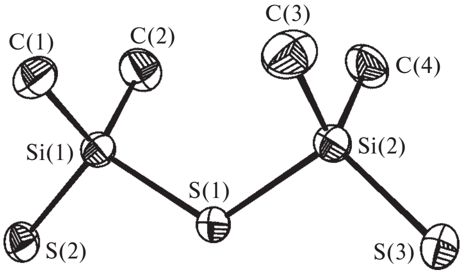


Fig. 6. Structure of the dianion of salt **49a**.

transformed into the corresponding dithiadisilolanes **47**, as in the case of photolysis of betaine **16a** performed under homogeneous conditions (see Scheme 21).

In all cases, the further transformations of silanethiones [$R^3R^4Si{=}S$] and ylides $R_3P{=}CR^1R^2$, which were generated upon decomposition of betaines **16**, afforded phosphonium *symm*-tetraorganodisilathiapropanedithiolates $[Ph_3PCHR^1R^2]^+{}_2[(R^3R^4SiS)_2S]^{2-}$ (**49**) labile in solutions. The $[Et_4P^+]_2[S{-}SiMe_2{-}S{-}SiMe_2{-}S]^{2-}$ salt (**49a**), which was obtained by the *in situ* treatment of $[Ph_3PCHMe_2]^+{}_2[(Me_2SiS)_2S]^{2-}$ with more basic ylide $Et_3P{=}CHMe$, was characterized by NMR spectroscopy and X-ray diffraction analysis. In the crystal of **49a**, the planar $[S{-}SiMe_2{-}S{-}SiMe_2{-}S]^{2-}$ dianion adopts a W-shaped configuration (Fig. 6). The terminal $Si{-}S^-$ bonds are somewhat longer than these bonds in the starting betaines, and the central Si—S distances agree well with the average value.[70]

The mechanism of formation of salts **49** remains to be elucidated. The phosphonium cations are generated because phosphorus ylides, which are derived from betaine upon the retro-Wittig-type decomposition, act as strong bases and cause the proton abstraction from other compounds present in the reaction mixture. Under the strictly identical thermal conditions, pyrolysis of nondeuterated betaine **16a** in pyridine-d_5 and selectively deuterated betaines, *viz.*, $Ph_3P^+CMe_2Si(CD_3)_2S^-$ (**16b**), $Ph_3P^+C(CD_3)_2SiMe_2S^-$ (**16c**), and $Ph_3P^+C(CD_3)_2Si(CD_3)_2S^-$ (**16d**), in pyridine-d_5 and nondeuterated pyridine afforded the $Ph_3P^+CMe_2H$ and $Ph_3P^+CMe_2D$ cations. From the ratio between the nondeuterated and deuterated cations (Table 3) it follows that both pyridine and all substituents in betaine serve as sources of protons in the formation of salts **49**. The possibility of proton abstraction from the phenyl groups at the phosphorus atom of ylide $Ph_3P{=}CMe_2$ [90] and high CH-acidity of the Me groups at the Si atom[91,92] were noted by other authors as well.

An increase in CH-acidity of substituents in betaines facilitates thermal decomposition according to the retro-Wittig-type reaction, which proceeds under milder conditions. Upon thermal decomposition of betaines **16**, the yields of dithiadisilolanes **47** are decreased and the yields of salts **49** are increased in the following series: $Ph_3P^+CMe_2SiMePhS^-$ (**16f**), $Ph_3P^+CMe_2SiMe_2S^-$ (**16a**), $Ph_3P^+CHMeSiMe_2S^-$ (**16k**), and $Ph_3P^+CMe_2SiMeBzS^-$ (**16e**).

Table 3. Ratio between the $[Ph_3P^+CHMe_2]$ and $[Ph_3P^+CDMe]$ cations in salts **49** prepared by thermolysis of betaines **16a—d** (100 °C, 5 h, conversion was ~80%) in pyridine-d_5 and pyridine-H_5 (in parentheses)*

Betaine	Relative yield	
	$Ph_3P^+CHMe_2$	$Ph_3P^+CDMe_2$
16a	64 (100)	36(0)
16b	35 (57)	65(43)
16c	46 (58)	54(42)
16d	36	64

* The Ph_3P : **49a** : **47a** ratio was 1 : 0.5 : 0.5 at 100 °C and 150 °C (conversion was ~100%).

Pyrolysis of betaine $Ph_3P^+CHMeSiMe_2SSiMe_2S^-$ (**17**) produced the $[Ph_3PCHMe]^+{}_2[(Me_2SiS^-)_2S]^{2-}$ salt (**49k**) in ~70% yield and dithiadisilolane $Me_2\underbrace{Si{-}CHMe{-}S{-}Me_2Si{-}S}$ (**47k**) in only 5.5% yield, whereas pyrolysis of betaine **16k** under the same conditions afforded this salt in only 49% yield and the yield of compound **47k** was increased to 23%. Hence, not only the acidity of the substituents in the starting betaine but also, apparently, intermediate betaines with the $^+P{-}C{-}(Si{-}S{-})_nSi{-}S^-$ skeleton play an important role in the formation of salts **49**. The latter are formed due to the insertion of short-lived silanethiones [$R^3R^4Si{=}S$] into the starting betaines **16** or by the bimolecular reaction following the path *b* (see Scheme 23).

The above-considered results indicate that thermal decomposition of betaines **16** in solutions under drastic conditions is, most likely, accompanied by a complex system of equilibrium and nonequilibrium processes involving phosphorus ylides, silanethiones **48**, and their cyclodimers.

Thermal decomposition of betaines containing the arsonium cationic center has been exemplified only by betaine $Ph_3As^+{-}CHPh{-}SiMe_2S^-$ (**22b**). It is worthy of note that its decomposition proceeded readily and selectively. In a pyridine solution, compound **22b** was virtually quantitatively transformed into the corresponding dithiadisilolane and Ph_3As at ~20 °C during several hours.[57] Photodecomposition of its alkyl analog **22a** is described in Section 5.1.1.

5.1.3. Alkylation and acetylation of betaines $^{(+)}P{-}C{-}Si{-}S^{(-)}$ (I)

Heating of a suspension of betaine **16a** in THF with bromoethane afforded salt **40** in 70% yield

(Scheme 25).[50,93] The results of X-ray diffraction analysis of this compound are presented in Section 4.

Scheme 25

$$\underset{\textbf{16a}}{Ph_3P^+\text{—}CMe_2\text{—}SiMe_2\text{—}S^-} \xrightarrow{EtBr}$$

$$\longrightarrow \underset{\textbf{40}}{[Ph_3P^+\text{—}CMe_2\text{—}SiMe_2\text{—}SEt]\,Br^-}$$

Alkylation of betaines, which contain the hydrogen atom at the α position with respect to the phosphonium center, with bromoethane proceeded differently to give a complex mixture of products. This reaction is considered in Section 5.1.5.

The reactions of betaines **16a,n** with acetyl chloride proceeded unusually.[93,94] The compositions and structures of the reaction products depend on the molar ratio of the reagents. The reaction of the reagents taken in an equimolar ratio in THF gave rise to cyclic compound **56** in 96—98% yield (Scheme 26).

Apparently, the initially formed S-acetyl derivative **51** underwent the rearrangement due to migration of the organosilicon fragment to the oxygen atom. This process is thermodynamically favorable. The second betaine molecule acts as a base and deprotonates thioacetate **52**. This type of deprotonation of thiocarbonyl compounds was described in the literature.[95] Acetylation of thioenolate ion **53** yielded β-thiocarbonyl compound **54**. Subsequent enolyzation and the formation of the extremely strong Si—O bond completed cyclization and the formation of 2-sila-1,3-dioxenethione **56**. As expected,[96] phosphonium salt **55** decomposed with the cleavage of the Si—C bond.

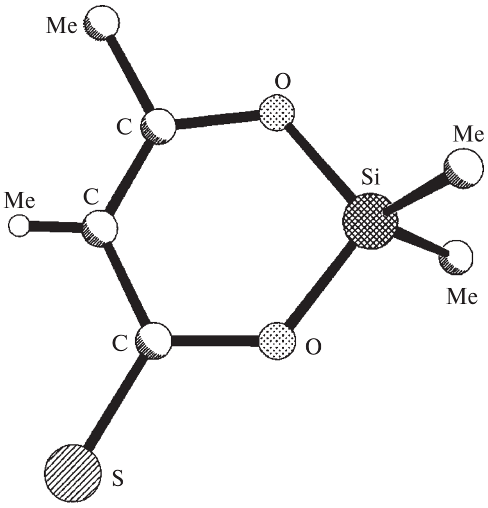
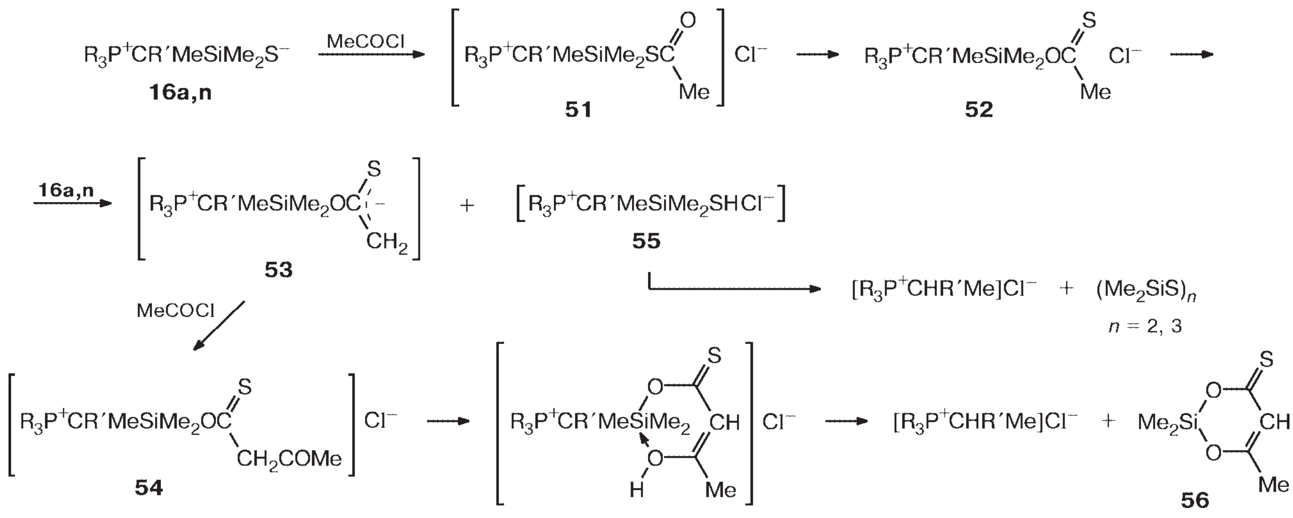


Fig. 7. Molecular structure of compound **56**.

According to the X-ray diffraction data (Fig. 7), the 2,2,6-trimethyl-1,3-dioxa-2-silacyclohex-5-ene-4-thione molecule (**56**) contains the planar strongly strained ring in which the tetrahedral geometry of the silicon atom is substantially distorted. The O—Si—O and C—Si—C bond angles (103.7(1)° and 115.1(1)°, respectively) differ substantially from the ideal tetrahedral value (109.5°) and the Si—O bond lengths (1.668(2) and 1.675(2) Å) are somewhat larger than the average value (1.645 Å).[70] Apparently, it is these distortions that are responsible for the very high reactivity of compound **56**, in particular, with respect to atmospheric oxygen and moisture.

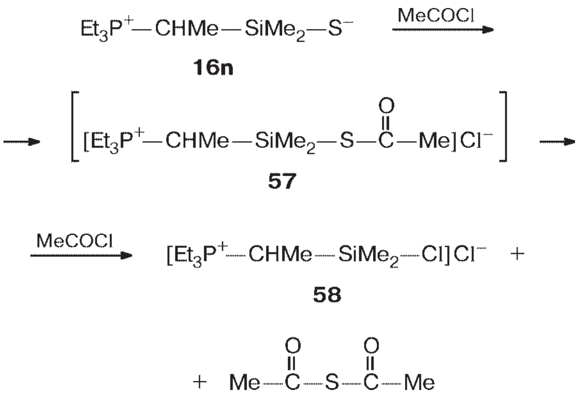
Scheme 26



R = Ph, R′ = Me (**a**); R = Et, R′ = H (**n**)

Heating of betaine **16n** with a large excess of acetyl chloride in ether afforded salt **58** in virtually quantitative yield (Scheme 27).[93,94]

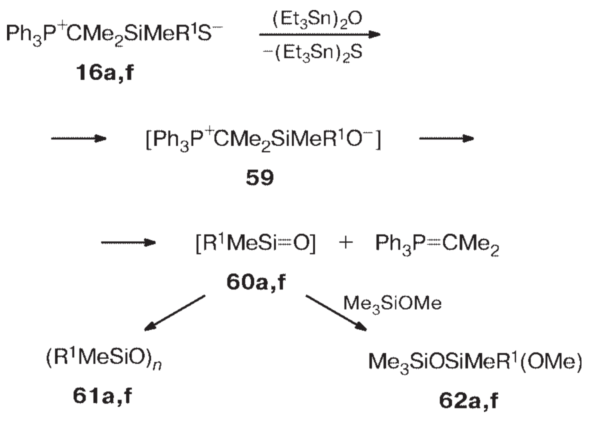
Scheme 27



5.1.4. Reactions of betaines $^{(+)}$P—C—Si—S$^{(-)}$ (I) with the $(R_3Sn)_2X$ compounds (X = O, NMe)

It is known that the $(R_3Sn)_2X$ compounds are readily involved in various exchange reactions.[54] Intermediate silicon-containing organophosphorus betaines **59** possessing the oxide anionic center were not detected in the reactions of betaines **16a,f** with $(R_3Sn)_2O$ in ether at ~20 °C.[93,97] In solutions, these intermediates underwent *in situ* retro-decomposition to produce highly reactive silanones **60**. The chemistry of the latter compounds has been extensively developed in recent years.[46,98,99] The existence of silanones **60** was established from the formation of cyclotrimers **61** and also based on the formation of methoxydisiloxanes **62** in the reaction with trimethylmethoxysilane, which is a good chemical trap of silanones (Scheme 28). Hence, the thermal stability of oxabetaines **59** is, most likely, much lower than that of their thio analogs whose decomposition under similar conditions proceeds at a noticeable rate only at temperatures higher than 50 °C.

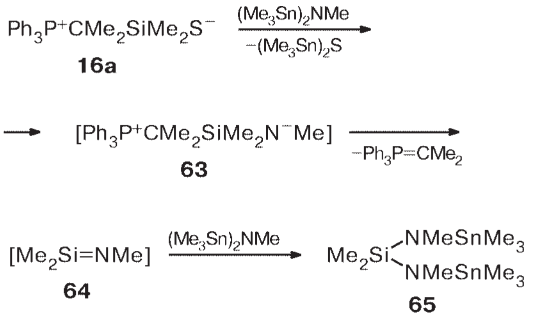
Scheme 28



R^1 = Me (**a**), Ph (**f**)

The reactions of silicon-containing organophosphorus betaines with bis(trimethylstannyl)methylamine proceed analogously.[93] Betaine **63** possessing the amide anionic center, which was, most likely, generated as an intermediate, decomposed to yield silaneimine **64**. An excess of bis(trimethylstannyl)methylamine acted as a trapping agent with respect to compound **64**. The reaction with the use of a twofold excess of organostannane afforded compound **65** in 90% yield (Scheme 29).

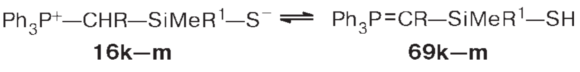
Scheme 29



5.1.5. Isomerization of organophosphorus betaines I containing the hydrogen atom at the α position with respect to the phosphonium center

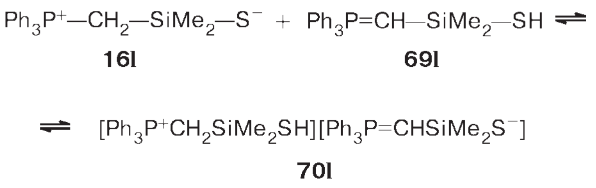
In solutions, betaines **16k—m** underwent isomerization into silylated phosphorus ylides **69** (Scheme 30).[75] This process was clearly followed by ^1H, ^{13}C, and ^{31}P NMR spectroscopy from the appearance of the signals characteristic of phosphorus ylides,[75,100] including those silylated at the ylide carbon atom.[75,101]

Scheme 30

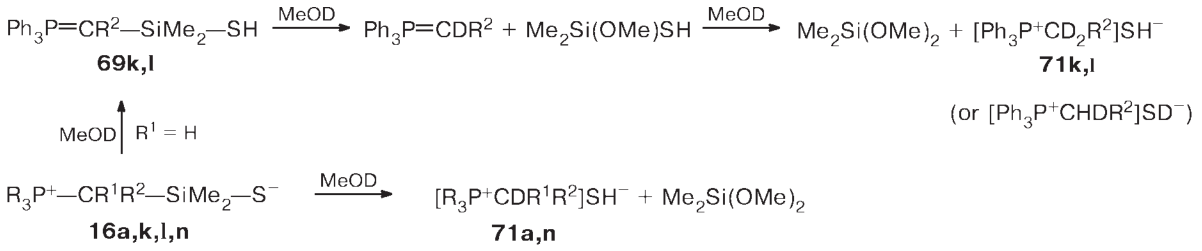


R = R^1 = Me (**k**); R = H, R^1 = Me (**l**); Ph (**m**)

Scheme 31



Scheme 32



	R	R^1	R^2
a	Ph	Me	Me
k	Ph	H	Me
l	Ph	H	H
n	Et	H	Me

An increase in the temperature or a decrease in the polarity of the solvent leads to the shift of the equilibrium to ylides **69**. Thus, in the synthesis of betaine **16k** in benzene, up to 62% of **69k** was detected in the solution along with betaine **16k**, whereas compound **16k** in pyridine was detected in amounts of at most 1.4% and 3.6 % at ~20 °C and 90 °C, respectively.

In solutions, isomerization of betaine **16l** into ylide **69l** was accompanied by the equilibrium processes of the intermolecular proton transfer between the thiolate center and the sulfhydryl group yielding salts of type **70** (Scheme 31), which was proved by ^{29}Si NMR spectroscopy.[76]

An equilibrium of this type has been observed previously in the studies of the reactions of alkylidenetriphenylphosphoranes with carbon disulfide.[102,103]

Isomerization of betaines **16** into silylated ylides was chemically confirmed in the study of the reactions of betaines **16** with bromoethane and alcohols.[76] Unlike the reaction of betaine **16a** containing the quaternary ylide carbon atom (see Scheme 25), the reaction of betaine **16k** with bromoethane afforded a complex mixture of products. In the latter case, the halide ion, which was eliminated upon alkylation of the thiolate center, acted as a nucleophile to cleave the C—Si bond in ylide **69k**. The resulting phosphorus ylide $Ph_3P=CHMe$ was involved in a series of subsequent transformations, which have been described for analogous systems in detail.[96] The reactions with betaine **16k** afforded $Ph_3P=C(Me)SiMe_2X$, $[Ph_3P^+C(H)MeSiMe_2X]Y^-$, Me_2SiXY (X and Y are Br or SEt), $[Ph_3P^+Et]Br^-$, and $Ph_3P=CHMe$ as the final products.[76]

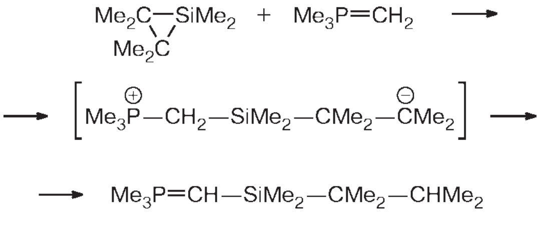
Isomerization of betaines **16k,l** into silylated phosphorus ylides was also confirmed by their reactions with methanol-d$_1$, which proceeded rather rapidly even at room temperature to give $Me_2Si(OMe)_2$ and a mixture of α-deuterated phosphonium salts **71k,l** (Scheme 32) among which doubly deuterated salts were obtained as the major products. Most likely, the reactions proceeded through the intermediate formation of α-silylated phosphorus ylides **69**. The subsequent transformations of these compounds in methanol-d$_1$ occurred according to the general schemes, which have been established for the reactions of alcohols with $R_3P=CHR^1$ (R^1 = H, Alk, or Me_3Si).[104,105]

Betaines possessing the trialkylphosphonium center do not virtually undergo isomerization into silylated ylides due to lower CH-acidity of the phosphonium salts of the alkyl series compared to aryl-substituted salts and, consequently, because of higher basicity (nucleophilicity) of their conjugated bases, *viz.*, phosphorus ylides.[105] No noticeable amounts of the doubly α-deuterated $[Et_3P^+CD_2Me]SH^-$ salt were detected upon alcoholysis of betaine $Et_3P^+CHMeSiMe_2S^-$ (**16n**) (see Scheme 32). Here, as in the case of betaine $Ph_3P^+CMe_2SiMe_2S^-$ (**16a**), which cannot undergo isomerization, only α-monodeuterated salt **71k** was identified in the products of slow alcoholysis.

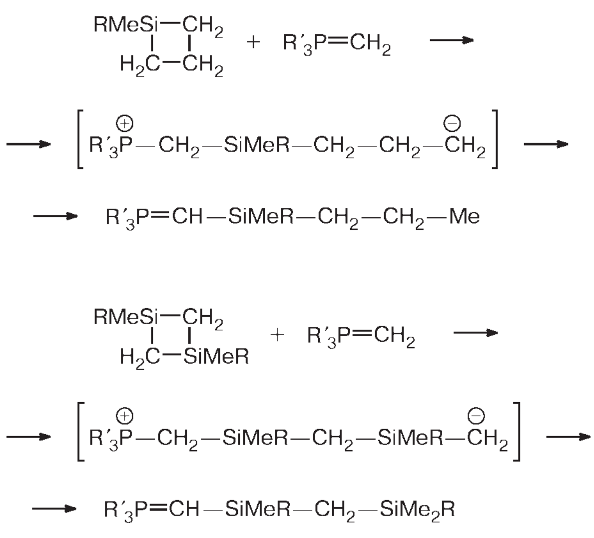
The intermediate formation of betaines and their subsequent irreversible isomerization into silylated phosphorus ylides has previously been postulated for the reactions of phosphorus ylides with hexamethylsilacyclopropane,[106] silacyclobutane,[107] and disilacyclobutane containing different substituents at the silicon atom (Schemes 33 and 34).[108]

The reaction of octaphenylcyclotetrasilane with phosphorus ylide can be described by Scheme 35.[109]

Scheme 33

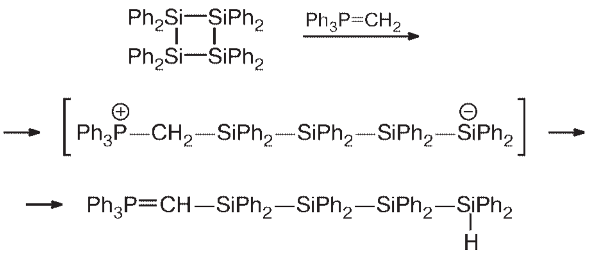


Scheme 34



R = H, Me; R′ = Me, Et, Pr^i.

Scheme 35



The reaction of octaphenylcyclotetrasilane with $Et_3P=CHMe$ proceeded analogously. The composition of the final product remained unchanged when the reagents were taken in a ratio of 1 : 4. Under the same conditions, $Ph_3P=CMe_2$ did not react with octaphenylcyclotetrasilane.[53]

5.1.6. Chemical transformations of betaines $^{(+)}P—C—Sn^{(-)}$ (II)

The data on the chemical properties of betaines **II** are scarce.

Thermolysis (105 °C) of betaine **27b** was found to afford cyclic dibetaine **41** (Scheme 36).[73]

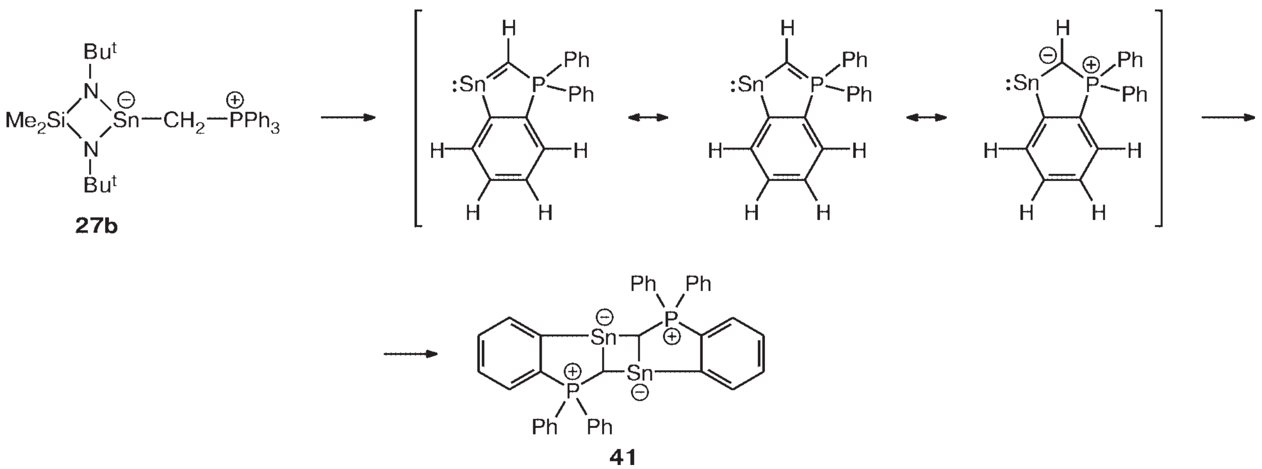
The reaction scheme proposed in the study[73] involves the formation of a hydrogen bond between the *ortho* proton of the phenyl ring and one of the nitrogen atoms of cyclostannylene followed by the cleavage of the Sn—N bond and the formation of the C—Sn bond. The second Sn—N bond is cleaved under the action of one of the protons of the CH_2 group bound to the phosphorus atom. This reaction scheme was confirmed by the study of the reaction kinetics and also by the formation of $Me_2Si(NDBu^t)(NHBu^t)$ upon pyrolysis of deuterated betaine $Ph_3P^+—CD_2—Sn(NBu^t)_2SiMe_2$.

Investigations of the reactivities of betaines of types **I** and **II** are far from being completed. The available data provide evidence that these compounds are involved in a broad range of reactions. Compounds of this type would be expected to find many synthetic applications, including those for the preparation or *in situ* generation of compounds with the $E^{14}=X$ double bonds.

6. Structures and reactivities of betaines of types I and II according to the results of theoretical calculations

Modern quantum-chemical methods, including the density functional theory, allow one to obtain reliable quantitative information on the structures and reactivities of heteroorganic compounds within reasonable cal-

Scheme 36



culation time.[110] We investigated the potential energy surfaces of betaines of types **I** and **II** in detail by the density functional theory using the generalized gradient approximation and the PBE functional proposed in the study.[111] The one-electron wave functions were expanded using the extended atomic basis sets of the grouped Gaussian functions of the types {311/1} for the H atom, {611111/411/11} for the C, N, and O atoms, {6111111111/5111111/11} for the Si, P, and S atoms, {7111111111111/5111111111/51111} for the Ge, As, and Se atoms, and {71111111111111111/5111111111111/61111111} for the Sn atom (the figures in braces represent the modes of grouping of the Gaussian functions for AOs with the *s*, *p*, and *d* symmetry). According to the algorithm proposed in the study,[112] the matrix elements of the Coulomb and exchange-correlation potentials were calculated using expansion of the electron density in an auxiliary basis set consisting of the atom-centered nongrouped Gaussian functions of the types (5*s*1*p*) for H, (10*s*3*p*3*d*1*f*) for C, N, and O, (14*s*7*p*7*d*1*f*1*g*) for Si, P, and S, (18*s*5*p*5*d*3*f*3*g*) for Ge, As, and Se, and (21*s*6*p*6*d*4*f*1*g*) for Sn. The stationary points on the potential energy surfaces of the systems under study were identified from analysis of the Hessian matrices. The second derivatives of the energy with respect to the coordinates were calculated analytically. The correction for the zero-point energy was calculated in the harmonic approximation. All calculations were carried out using the original PRIRODA program created by D. N. Laikov.[113]

6.1. Molecular geometry of betaines $^{(+)}E^{15}$—C—E^{14}—$S^{(-)}$. Comparison of the calculated data with the results of X-ray diffraction analysis

The geometric parameters of the main structural fragment $^{(+)}E^{15}$—C—E^{14}—$S^{(-)}$, which were calculated for a series of betaines of type **I** studied by X-ray diffraction analysis (see Section 3), are given in Table 4. The data obtained from X-ray diffraction analysis are given in parentheses.[114]

The results of calculations are in satisfactory qualitative agreement with the experimental data. The calculations adequately reproduce the major characteristic structural feature of all betaines, *viz.*, their sterically strained *gauche* conformation, which occurs due to strong Coulomb interactions between the cationic and anionic centers. The calculated covalent bond lengths in the $^{(+)}E^{15}$—C—E^{14}—$S^{(-)}$ fragment are somewhat overestimated (by less than 0.06 Å) compared to the experimental values. These discrepancies may be attributed to the crystal packing effects, which are generally pronounced in the presence of polar bonds. The peripheral C—C, E^{15}—C, and C—E^{14} bond lengths are reproduced with a higher accuracy (the discrepancies are no larger than 0.04 Å). The calculated C—E^{14}—S and E^{15}—C—E^{14} bond angles and the E^{15}—C—E^{14}—S dihedral angles are slightly underestimated compared to the experimental data. More substantial discrepancies are observed for the dihedral angles, which are associated with the fact that the intermolecular Coulomb interactions in the crystal compete with the intramolecular Coulomb interactions between the thiolate anionic and phosphonium (arsonium) cationic centers. The results of calculations also adequately reproduce the structural characteristic feature of arsonium betaine **22a** mentioned in Section 3. Thus, the geometry of the arsenic atom can be considered as intermediate between a distorted tetrahedron and a trigonal bipyramid due to the presence of the short As—S contact.

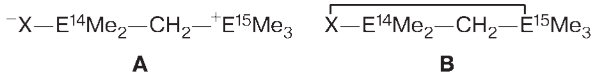
6.2. Potential energy surfaces of model betaines $^{(+)}Me_3E^{15}$—CH_2—$E^{14}Me_2$—$X^{(-)}$ (E^{15} = P, As; X = S, C_5H_4, O, NMe, Se)

Potential energy surfaces for betaines **I** were examined using the model $^{(+)}Me_3E^{15}$—CH_2—$E^{14}Me_2$—$X^{(-)}$ compounds (E^{15} = P or As; X = S, Se, C_5H_4, O, or NMe). The replacements of the radicals at the heteroatoms in the betaine molecules by the methyl groups allow one to substantially reduce the calculation time, while the model systems retain the reasonable similarity to the

Table 4. Geometric parameters of the $^{(+)}E^{15}$—C—E^{14}—$S^{(-)}$ fragment for betaines possessing the thiolate center according to the results of DFT calculations and X-ray diffraction analysis (X-ray data are given in parentheses)

Betaine	*r*/Å				φ/deg		θ/deg
	E^{15}—C	C—E^{14}	E^{14}—S	E^{15}—S	E^{15}—C—E^{14}	C—E^{14}—S	E^{15}—C—E^{14}—S
Ph_3P^+—CMe_2—$SiMe_2$—S^-	1.865	2.037	2.064	3.687	111.7	111.9	36.7
	(1.825)	(1.986)	(2.048)	(3.988)	(115.60)	(114.6)	(56.1)
Et_3P^+—CHMe—$SiPh_2$—S^-	1.827	1.993	2.063	3.527	110.1	110.9	32.9
	(1.811)	(1.934)	(2.044)	(3.681)	(112.8)	(114.7)	(38.2)
Et_3As^+—CHPh—$SiMe_2$—S^-	1.986	1.969	2.083	3.040	105.1	102.0	24.4
	(1.936)	(1.946)	(2.0455)	(3.518)	(111.47)	(109.97)	(33.13)
Et_3P^+—CHMe—$GeMe_2$—S^-	1.815	2.108	2.157	3.642	110.8	111.2	26.0
	(1.783)	(2.041)	(2.140)	(3.967)	(114.3)	(114.9)	(25.9)

Table 5. Betaine (**A**) and cyclic (**B**) forms of the model $X—E^{14}Me_2—CH_2—E^{15}Me_3$ compounds (X = S, Se, C_5H_4, O, or NMe; E^{14} = Si, Ge, or Sn; E^{15} = P or As)


$^{-}X—E^{14}Me_2—CH_2—^{+}E^{15}Me_3$ $X—E^{14}Me_2—CH_2—E^{15}Me_3$

A **B**

E^{14}	X—E^{15}							
	S—P	S—As	Se—P	Se—As	O—P	O—As	N—P	N—As
Si	b	b	b	b	b+c	c	b+c	c
Ge	b	b	b	b	b+c	c	b+c	c
Sn	b	b	b	b	b+c	c	b+c	b+c

Note: b, only the betaine form is observed on PES; c, only the cyclic form is observed on PES; b+c — both the betaine and cyclic forms are possible.

real molecules for which the experimental data are available.[52,53,57,114,115]

6.2.1. Open and cyclic forms. Conformations with respect to the $CH_2—E^{14}$ bond

As mentioned in Sections 1 and 5, the determination of the relative stabilities of betaines with open structures and of cyclic oxaphosphetanes as intermediates was among the most important problems in studies of the mechanism of the Wittig reaction. The solution of the analogous problem in the chemistry of heteroorganic betaines **I** was of obvious interest. In this connection, the region of potential energy surfaces of the model betaines corresponding to rotation about the central $CH_2—E^{14}$ bond was examined in detail and the minima corresponding to cyclic isomers were searched for.

All the model compounds under study can be readily divided into three groups (Table 5). The first group includes compounds containing the sulfur or selenium atom or the cyclopentadienyl anion as the anionic centers. These compounds exist only in the open betaine forms and no local minima corresponding to cyclic isomers are observed on their potential energy surfaces (PES).

The second group comprises compounds possessing the arsonium cationic center and the oxide anionic center as well as silicon- and germanium-containing betaines with the arsonium and amide centers. These compounds exist as cyclic isomers and their PES reveal no local minima corresponding to the open forms. Finally, the third groups involves six compounds possessing the phosphonium cationic center and the oxide or amide anionic center as well as arsonium imide betaine. Their PES have minima corresponding to the cyclic and open forms separated by low barriers.

For all betaines of the first group and also for the open forms of the third group, the *gauche* conformation is most stable. The principal geometric parameters of these betaines are given in Table 6. The dipole moments of betaines of the first and third groups are listed in Table 7. The potential energy surfaces of betaines $^{(+)}Me_3E^{15}—CH_2—E^{14}Me_2—X^{(-)}$ (E^{15} = P or As; E^{14} = Si or Ge; X = S, Se, or C_5H_4) have also local minima corresponding to the *trans* conformers. The principal

Table 6. Principal geometric parameters of the *gauche* conformers of betaines of the first group

Betaine	r/Å						φ/deg		θ/deg
	X—E^{14}	E^{14}—C	E^{14}—C_{Me}	C—E^{15}	X...E^{15}	E^{14}...E^{15}	X—E^{14}—C	E^{14}—C—E^{15}	X—E^{14}—C—E^{15}
P—C—Si—S	2.065	2.003	1.904	1.794	3.584	3.196	111.8	114.6	20.8
P—C—Ge—S	2.154	2.106	1.988	1.788	3.658	3.277	111.7	114.3	0.8
P—C—Sn—S	2.338	2.324	2.196	1.782	3.815	3.452	108.1	113.8	0.0
As—C—Si—S	2.071	1.974	1.905	1.928	3.403	3.213	108.4	110.9	23.2
As—C—Ge—S	2.159	2.078	1.987	1.920	3.530	3.312	109.3	111.8	9.7
As—C—Sn—S	2.341	2.304	2.196	1.912	3.740	3.504	107.0	112.1	0.2
P—C—Si—Se	2.211	1.997	1.907	1.796	3.733	3.214	112.3	115.7	26.0
P—C—Ge—Se	2.294	2.102	1.988	1.789	3.807	3.292	112.7	115.4	12.1
P—C—Sn—Se	2.467	2.324	2.196	1.782	3.968	3.467	109.5	115.1	0.1
As—C—Si—Se	2.217	1.971	1.906	1.929	3.563	3.239	109.1	112.4	27.5
As—C—Ge—Se	2.299	2.074	1.987	1.920	3.689	3.328	110.1	112.8	19.2
As—C—Sn—Se	2.471	2.305	2.196	1.911	3.896	3.530	108.6	113.4	0.1
P—C—Si—O	1.599	2.012	1.907	1.794	2.994	3.070	106.0	107.4	0.2
P—C—Ge—O	1.721	2.114	1.989	1.789	3.097	3.152	105.1	107.4	0.6
P—C—Sn—O	1.931	2.325	2.198	1.787	3.218	3.332	100.4	107.6	0.1
P—C—Si—N	1.680	1.981	1.918	1.797	3.042	3.141	102.8	112.4	6.4
P—C—Ge—N	1.801	2.070	2.004	1.794	3.120	3.212	101.8	112.3	0.8
P—C—Sn—N	2.012	2.293	2.214	1.788	3.245	3.402	97.3	112.4	1.9
As—C—Sn—N	2.011	2.270	2.215	1.919	3.100	3.446	94.4	110.4	0.2
P—C—Si—C_5H_4	1.822	1.988	1.899	1.802	3.489	3.208	109.1	115.6	32.3

Table 7. Dipole moments of the *gauche* conformers of betaines of the first and third groups

Betaine	μ/D	Betaine	μ/D
P—C—Si—S	9.7	As—C—Si—Se	9.6
P—C—Ge—S	9.6	As—C—Ge—Se	9.8
P—C—Sn—S	9.6	As—C—Sn—Se	9.9
As—C—Si—S	9.2	P—C—Si—O	7.8
As—C—Ge—S	9.4	P—C—Ge—O	7.6
As—C—Sn—S	9.6	P—C—Sn—O	7.5
P—C—Si—Se	10.1	P—C—Si—N	7.5
P—C—Ge—Se	9.9	P—C—Ge—N	7.4
P—C—Sn—Se	10.0	P—C—Sn—N	7.2
P—C—Si—C_5H_4	10.5	As—C—Sn—N	7.0

geometric parameters of the *trans* conformations of these betaines, their relative energies, and dipole moments are given in Table 8.

Analysis of the data presented in Tables 6—8 for betaines of the first group clearly shows the following regularities.

1. The E^{15}—C—E^{14}—X torsion angles in phosphonium and arsonium betaines are decreased in the series E^{14} = Si > Ge > Sn. This fact is undoubtedly associated with an increase in the length of the central E^{14}—C bond in the same order resulting in weakening of all repulsive interactions in the eclipsed conformation.

2. The central E^{14}—C bonds are noticeably longer (~0.1 Å) than the E^{14}—C_{Me} bonds and the E^{14}—C—E^{15} bond angles are larger than the ideal tetrahedral value (109.5°), which is indicative of the presence of substantial steric strains caused by very short X...E^{15} nonbonded contacts. For tin-containing betaines, the X...E^{15} distances approach the sum of the van der Waals radii (Table 9). This regularity is clearly manifested in the experimental data obtained by X-ray diffraction analysis (see Section 3).

3. It is characteristic that the interatomic E^{14}...E^{15} distances in the model betaines are 0.6—0.8 Å smaller than the sums of the corresponding van der Waals radii (see Table 9). This also leads to an increase in steric strains in the *cis* conformers.

4. The dipole moments of betaines (see Table 7) range from 9.2 to 10.1 D. These compounds are strongly polar and must exist as crystals in the free state.

5. The barriers to rotation about the central E^{14}—C bond are in the range of 11.6—13.0 kcal mol^{-1}.

6. The energies of the *trans* conformers of betaines $^{(+)}Me_3E^{15}$—CH_2—$E^{14}Me_2$—$X^{(-)}$ (E^{15} = P or As; E^{14} = Si or Ge; X = S, Se, or C_5H_4) are 11.3—12.7 kcal mol^{-1} higher than those of the corresponding *cis* conformers, the X—E^{14}—C and E^{14}—C—E^{15} bond angles being substantially decreased to 102.4—104.1° and increased to 121.8—123.4°, respectively. The dipole moments are increased to 14.0—14.4 D due to an increase in the $^{(-)}X...E^{15(+)}$ distance between the charged centers to 4.9—5.2 Å.

The energies of the O—As and N—As covalent bonds are higher than those of the S—As and Se—As bonds by approximately 25 kcal mol^{-1}, which is favorable for the closure of the strained four-membered rings in arsonium betaines with X = O or NMe because the gain in the energy due to the formation of the O—As and N—As bonds overrides the destabilization effect of the formation of small rings. The structural parameters of the rings in the compounds of the second group and of the cyclic isomers of the third group are given in Table 10.

In the compounds of the second group and cyclic isomers of the third group, the configuration at the E^{15} atoms differs from that observed in their betaine analogs. In these compounds, the phosphorus and arsenic atoms have a trigonal-bipyramidal configuration with the X atom and one of the methyl groups in the axial positions. The carbon atom of the E^{15}—C—E^{14}—X main chain and two methyl groups are located in the equatorial positions. The E^{15}—C bonds with the carbon atom of the methyl group in the axial position are 0.05—0.08 Å longer than the corresponding bonds with the carbon atom in the equatorial position. The E^{15} atom deviates from the equatorial plane toward the axial methyl group by 0.03—0.06 Å.

Table 8. Geometric parameters, dipole moments, and relative energies of the *trans* conformers of betaines of the first group

Betaine	r/Å				φ/deg		θ/deg	ΔE^0 /kcal mol^{-1}	μ/D
	X—E^{14}	E^{14}—C	C—E^{15}	X...E^{15}	X—E^{14}—C	E^{14}—C—E^{15}	X—E^{14}—C—E^{15}		
P—C—Si—S	2.034	2.015	1.783	4.891	104.8	123.4	159.2	11.8	14.1
P—C—Ge—S	2.119	2.127	1.772	4.967	103.8	122.4	150.4	12.3	14.0
P—C—Si—Se	2.179	2.011	1.786	5.009	104.8	123.2	158.4	11.3	14.3
P—C—Ge—Se	2.259	2.121	1.775	5.089	103.9	122.3	151.7	11.7	14.3
As—C—Si—S	2.037	1.992	1.927	4.997	103.6	122.1	163.0	12.1	14.1
As—C—Ge—S	2.121	2.099	1.914	5.096	102.6	121.8	159.0	12.7	14.2
As—C—Si—Se	2.182	1.986	1.934	5.118	103.3	122.0	163.4	11.6	14.4
As—C—Ge—Se	2.261	2.093	1.919	5.213	102.4	121.8	159.7	12.0	14.4

Table 9. Sums of the van der Waals (R_{WW}) and covalent (R_c) radii for the pairs of the E^{14}, E^{15}, and X atoms

Atomic pair	ΣR_c	ΣR_{WW}	Atomic pair	ΣR_c	ΣR_{WW}
	Å			Å	
S—P	2.14	3.75	N—As	1.91	3.54
S—As	2.25	3.85	Si—P	2.27	3.90
Se—P	2.27	3.90	Si—As	2.38	4.00
Se—As	2.38	4.00	Ge—P	2.32	3.90
O—P	1.76	3.30	Ge—As	2.43	4.00
O—As	1.87	3.40	Sn—P	2.50	4.10
N—P	1.80	3.44	Sn—As	2.61	4.20

Yet another characteristic feature of the cyclic isomers of betaines is a decrease in the X—E^{14}—C bond angle in the series Si, Ge, and Sn from 85.1—93.5° for silicon to 74.6—81.2° for tin. This is associated with the fact that the energy of destabilization caused by a change in the bond angle decreases as the atomic number in the above series increases. This effect is well known for compounds containing four-membered rings in which atoms characterized by substantially different electronegativities alternate with each other.

The energies of the O—P and N—P bonds are approximately 15 kcal mol^{-1} lower than those of the O—As and N—As bonds. Hence, PES for the compounds of the third group (E^{15} = P; X = O or NMe) have minima corresponding to both possible forms, *viz.*, to the open betaine and cyclic forms. This group involves also a compound of the arsonium series bearing the amide anionic center (E^{14} = Sn, E^{15} = As, X = NMe). The cyclic isomer of the latter compound is destabilized to a greater extent than the germanium- and silicon-containing rings due to the very short nonbonded contact between the As and Sn atoms; the distance between these atoms is 0.75 Å smaller than the sum of their van der Waals radii (see Table 10).

The barriers to rotation about the central E^{14}—C bond in betaines of the third group are in the range of 15.3—18.2 kcal mol^{-1}, the height of the barrier being increased in the series Si < Ge < Sn and on going from X = O to X = NMe.

In the compounds of the third group, the energies of the cyclic isomers are always lower than those of the open betaine forms. The relative energies and activation barriers are given in Table 11. It should be emphasized that the cyclic isomers of betaines of the second and third groups are much less polar than the corresponding betaines. The dipole moments are in the range of 4.5—5.6 D. For betaines of this group, the gain in the energy upon the formation of the cyclic forms ranges from 0.5 to 10 kcal mol^{-1}. Hence, it can be concluded that the cyclic forms in solutions can exist in the dynamic equilibrium with the open forms of betaines, the position of the equilibrium being substantially affected by the polarity of the medium. The equilibrium is shifted to the more polar open forms as the polarity of the medium is increased.

6.2.2. Main pathways of decomposition and isomerization of betaines I

Of four main pathways of chemical transformations involving betaines of the first group (see Scheme 37), isomerization to give metallated ylides (path *a*), retro-Wittig-type decomposition (path *b*), and Corey—Chaykovsky-type decomposition (path *c*) giving rise to compounds with a three-membered ring (see Section 5) have been discovered experimentally. Of paramount interest is also Wittig-type decomposition (path *d*), which is as yet not observed under experimental conditions. When studying these processes by experimental and theoretical methods, it should be realized that the possibility of these processes occurring also depends heavily on the subsequent reactions, which can involve

Table 10. Geometric parameters of the cyclic $\overline{X—E^{14}Me_2—CH_2—E^{15}}Me_3$ compounds of the second and third groups

Betaine	r/Å						φ/deg		θ/deg
	X—E^{14}	E^{14}—C	E^{14}—C_{Me}	C—E^{15}	X—E^{15}	E^{14}...E^{15}	X—E^{14}—C	E^{14}—C—E^{15}	X—E^{14}—C—E^{15}
P—C—Si—O	1.654	1.910	1.894	1.867	2.006	2.739	89.6	92.9	0.0
P—C—Ge—O	1.798	1.976	1.972	1.885	1.901	2.808	84.1	93.3	0.0
P—C—Sn—O	2.008	2.176	2.181	1.894	1.860	2.994	76.6	94.4	0.1
As—C—Si—O	1.646	1.924	1.897	1.979	2.164	2.838	93.5	93.3	0.1
As—C—Ge—O	1.787	1.989	1.975	1.997	2.068	2.900	88.4	93.4	0.0
As—C—Sn—O	1.996	2.188	2.184	2.006	2.037	3.079	81.2	94.4	0.0
P—C—Si—N	1.731	1.894	1.899	1.889	1.926	2.795	85.1	95.2	0.8
P—C—Ge—N	1.844	1.969	1.978	1.896	1.898	2.880	81.1	96.3	3.7
P—C—Sn—N	2.049	2.172	2.191	1.897	1.892	3.074	74.6	97.9	2.4
As—C—Si—N	1.727	1.901	1.902	2.006	2.075	2.890	89.0	95.4	0.2
As—C—Ge—N	1.843	1.973	1.979	2.016	2.048	2.967	85.1	96.1	6.7
As—C—Sn—N	2.047	2.176	2.193	2.017	2.043	3.156	78.6	97.6	4.7

Table 11. Relative energies (ΔE^0/kcal mol^{-1}) of the cyclic isomers and activation energies ($E_a{}^0$/kcal mol^{-1}) for the interconversions of the open and cyclic isomers of compounds of the third group

Betaine	$-\Delta E^0$	$E_a{}^0$	Betaine	$-\Delta E^0$	$E_a{}^0$
P—C—Si—O	0.5	0.9	P—C—Ge—N	9.4	1.3
P—C—Ge—O	4.3	0.9	P—C—Sn—N	6.8	2.9
P—C—Sn—O	3.5	2.6	As—C—Sn—N	10.9	0.1
P—C—Si—N	8.8	0.1			

the initially formed decomposition products. Among these reactions, the highly exothermic dimerization (oligomerization) reactions of compounds possessing the $X{=}E^{14}$ bonds and of three-membered heterocycles involving the E^{14} atoms are of most importance. Since the starting betaines and compounds with the $X{=}E^{14}$ bonds are highly polar and prone to complex formation, the solvation effects must also be taken into account.

6.2.3. Isomerization of betaines I into metallated phosphorus and arsenic ylides (path a)

The energies of ylides $HX{-}E^{14}Me_2{-}CH{=}E^{15}Me_3$ (X = S or Se; E^{14} = Si or Ge; E^{15} = P or As) are always higher than those of isomeric betaines. The differences in the energy are virtually independent of the nature of the E^{14} atom and are determined only by the type of ylide. These differences are in the range of 12—16 kcal mol^{-1} for phosphorus ylides and in the range of 15—21 kcal mol^{-1} for arsenic ylides possessing higher basicity and nucleophilicity. Ylides with X = O and E^{15} = P are comparable in stability with betaines or even more stable, whereas the energies of ylides with X = O and E^{15} = As are 2—9 kcal mol^{-1} higher than those of the cyclic forms. The energies of isomeric imide betaines with X = NMe of the ylide series are always 2—20 kcal mol^{-1} lower than those of the corresponding open and cyclic forms.

In ylides $HX{-}E^{14}Me_2{-}CH{=}E^{15}Me_3$, the central fragment retains the *gauche* conformation typical of betaines. The Coulomb interaction between the X atom bearing a partial negative charge and the positively charged arsenic or phosphorus atoms is retained although it is noticeably weakened as compared to that in the corresponding betaines. Hence, the barriers to rotation about the $E^{14}{-}C$ bonds in the ylides under consideration are ~5 kcal mol^{-1}, which are substantially lower than those in isomeric betaines. The dipole moments of ylides $HX{-}E^{14}Me_2{-}CH{=}E^{15}Me_3$ (μ ~ 3—5 D) are essentially lower than those of the corresponding betaines (μ ~ 7—10 D). Hence, the equilibrium between the betaine and ylide forms in low-polarity media must be shifted to the ylide. This shift was experimentally observed for silicon-containing organophosphorus betaines containing the thiolate anionic center (see Section 5). We believe that these processes follow an intermolecular mechanism involving donor solvent molecules or the second betaine molecule.

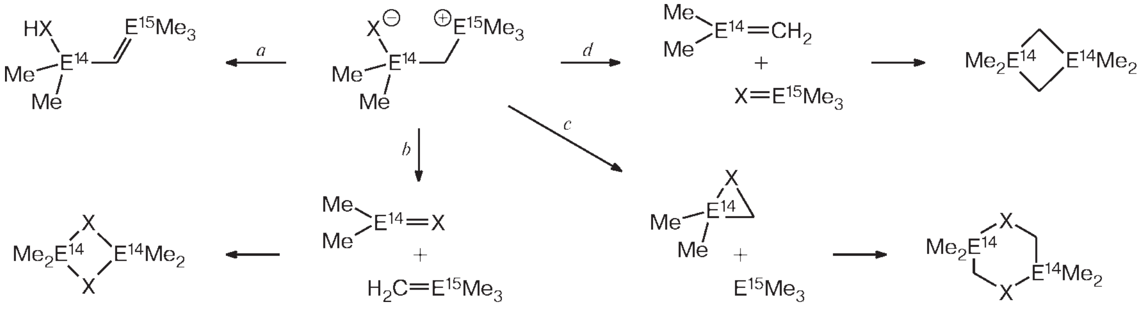
6.2.4. Retro-Wittig-type decomposition of betaines I (path b)

Under the gas-phase conditions, monomolecular retro-Wittig-type decomposition of betaines $^{(-)}X{-}E^{14}Me_2{-}CH_2{-}E^{15}Me_3{}^{(+)}$ proceeds as the simple cleavage of the central $E^{14}{-}C$ bond and, hence, it is a highly endothermic process (Table 12). High thermal stability of betaines **16o** and **16p** containing the alkyl groups at the phosphorus atom (see Section 5) is consistent with the above-mentioned data.

However, the $Me_2E^{14}{=}X$ compounds (E^{14} = Si, Ge, or Sn; X = O, S, Se, or NMe) generated by retro-Wittig-type decomposition are kinetically unstable and undergo exothermic cyclooligomerization to form dimers and trimers, which can compensate to a large extent the energy expended for this decomposition.

The tendency of the $Me_2E^{14}{=}X$ compounds to form stable complexes through coordination at the E^{14} atom of the donor molecules or *via* intramolecular coordination of the donor groups is well known and was already mentioned in Section 5. In this connection, the model

Scheme 37



X = S, Se, O, NMe; E^{14} = Si, Ge, Sn; E^{15} = P, As.

Table 12. Activation energies (E_a^0) and energies of the reactions (ΔE^0) for the major pathways of decomposition of betaines of type **I*** shown in Scheme 37

Betaine	Reaction pathway									
	a	*b*			*c*			*d*		
	Ylide	E_a^0	ΔE^0		E_a^0	ΔE^0		E_a^0	ΔE^0	
			$Me_2E^{14}{=}X$	Dimer		$Me_2E^{14}(X)CH_2$	Dimer		$Me_2E^{14}{=}CH_2$	Dimer
P—C—Si—S	12.3	— (17.8)	43.0 (21.7)	9.9	32.6	19.8	0.3	37.4	34.0 (27.2)	−5.1
P—C—Ge—S	12.0	— —	38.2 (22.1)	8.1	35.5	20.0	−1.6	32.2	28.9 (25.0)	−5.7
P—C—Sn—S	13.1	— —	40.2 (22.0)	5.1	41.6	24.7	1.4	35.2	38.4 (30.9)	−0.5
As—C—Si—S	16.4	— (21.1)	47.2 (25.9)	14.0	20.7	5.9	−16.6	29.7	35.3 (28.4)	−3.8
As—C—Ge—S	15.7	— —	41.7 (25.6)	11.6	22.9	5.3	−16.2	27.1	29.6 (25.7)	−5.1
As—C—Sn—S	16.3	— —	43.2 (25.0)	8.1	27.9	9.6	−13.6	29.0	38.5 (31.0)	−0.4
P—C—Si—Se	14.6	— (18.5)	42.9 (22.0)	12.3	30.1	19.4	1.4	35.4	35.1 (28.2)	−4.0
P—C—Ge—Se	15.6	— —	37.6 (21.9)	9.2	33.1	20.5	0.3	35.6	32.5 (28.6)	−2.2
P—C—Sn—Se	18.0	— —	39.2 (21.4)	6.3	39.8	26.5	4.3	40.1	44.1 (36.6)	5.2
As—C—Si—Se	18.9	— (21.9)	47.2 (26.3)	16.6	18.2	5.5	−12.5	28.4	32.9 (26.0)	−6.2
As—C—Ge—Se	19.3	— —	41.3 (25.6)	12.9	20.7	6.0	−14.2	27.8	29.7 (25.9)	−4.9
As—C—Sn—Se	21.2	— —	42.3 (24.5)	9.4	26.1	11.6	−10.7	31.6	40.7 (33.3)	1.9
P—C—Si—O	0.8	— —	44.6 (21.8)	−2.9	42.3	29.3	−1.0	—	28.2 (21.4)	−10.9
P—C—Ge—O	−4.6	— —	39.9 (22.5)	−0.7	42.3	21.2	−8.7	5.5	8.5 (4.6)	−26.2
P—C—Sn—O	−8.7	— —	43.5 (23.9)	−3.1	46.3	16.0	−10.7	1.2	8.5 (1.0)	−30.4
As—C—Si—O*	8.8	— —	52.4 (29.6)	4.9	33.5	19.1	−11.3	—	50.2 (43.4)	11.1
As—C—Ge—O*	6.2	— —	50.8 (33.4)	10.2	37.1	13.9	−16.1	—	33.3 (29.4)	−1.3
As—C—Sn—O*	1.8	— —	54.0 (34.4)	7.4	40.6	8.5	−18.2	—	33.2 (25.7)	−5.7
P—C—Si—N	−16.8	— —	33.3 (21.0)	−13.2	29.7	5.4	−25.2	—	26.5 (19.6)	−12.6
P—C—Ge—N	−18.1	— —	27.5 (19.7)	−9.2	31.2	1.5	−29.6	—	13.3 (9.4)	−21.3
P—C—Sn—N	−19.6	— —	31.6 (21.1)	−8.6	16.9	−4.9	−28.9	1.6	14.9 (7.5)	−23.9
As—C—Si—N*	−1.1	— —	48.8 (36.5)	2.3	28.4	2.9	−27.7	—	49.5 (42.7)	10.4
As—C—Ge—N*	−2.0	— —	43.4 (35.6)	6.7	30.3	−0.8	−31.9	—	36.7 (32.8)	2.0
As—C—Sn—N	−16.0	— —	34.8 (24.3)	−5.4	22.6	−19.7	−43.7	—	25.7 (18.3)	−13.2

* All values were calculated relative to the energies of the open (betaine) forms, except for the compounds of the second group (marked with asterisks) for which the open forms are unavailable. In the latter cases, the energies were calculated with respect to the cyclic forms. The dash signifies that the state is absent on PES. The values in parentheses refer to the corresponding reactions in the presence of one pyridine molecule.

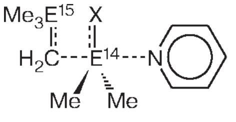
Table 13. Geometric parameters of the $Me_2E^{14}{=}X$ compounds (E^{14} = Si, Ge, or Sn; X = S, Se, O, NMe, or CH_2) and their complexes with pyridine $[Me_2E^{14}{=}X]\cdot Py$ (the values in parentheses) and the energies of complex formation (ΔE^0/kcal mol^{-1})

$Me_2E^{14}{=}X$	*d*/Å			φ/deg			$-\Delta E^0$
	E^{14}—X	E^{14}—C	E^{14}—N	X—E^{14}—C	C—E^{14}—C	X—E^{14}—N	
$Me_2Si{=}S$	1.978	1.883	—	124.5	111.0	—	
	(2.022)	(1.899)	(2.011)	(119.7)	(109.2)	(106.3)	21.3
$Me_2Ge{=}S$	2.060	1.968	—	123.9	112.1	—	
	(2.103)	(1.981)	(2.173)	(121.0)	(110.3)	(103.5)	16.1
$Me_2Sn{=}S$	2.260	2.182	—	124.6	110.8	—	
	(2.293)	(2.190)	(2.382)	(123.4)	(108.9)	(99.9)	18.2
$Me_2Si{=}Se$	2.123	1.884	—	124.6	110.8	—	
	(2.164)	(1.900)	(2.010)	(119.4)	(109.3)	(107.0)	20.9
$Me_2Ge{=}Se$	2.191	1.969	—	124.2	111.7	—	
	(2.240)	(1.981)	(2.170)	(120.9)	(110.0)	(104.5)	15.7
$Me_2Sn{=}Se$	2.383	2.183	—	124.9	110.3	—	
	(2.420)	(2.191)	(2.385)	(123.5)	(108.5)	(101.1)	17.8
$Me_2Si{=}O$	1.551	1.879	—	123.7	112.5	—	
	(1.572)	(1.898)	(2.013)	(120.6)	(109.4)	(101.5)	22.8
$Me_2Ge{=}O$	1.661	1.969	—	122.9	114.1	—	
	(1.685)	(1.981)	(2.184)	(121.4)	(111.2)	(97.8)	17.4
$Me_2Sn{=}O$	1.874	2.186	—	124.0	112.0	—	
	(1.896)	(2.194)	(2.384)	(123.7)	(109.7)	(92.5)	19.6
$Me_2Si{=}NMe$	1.622	1.875	—	117.7	117.3	—	
	(1.638)	(1.887)	(2.073)	(115.4)	(111.1)	(103.8)	12.3
$Me_2Ge{=}NMe$	1.729	1.980	—	127.7	115.9	—	
	(1.744)	(1.963)	(2.387)	(115.4)	(113.9)	(100.1)	7.8
$Me_2Sn{=}NMe$	1.948	2.174	—	115.4	115.0	—	
	(1.963)	(2.180)	(2.505)	(114.7)	(111.8)	(95.1)	10.5
$Me_2Si{=}CH_2$	1.722	1.884	—	122.7	114.6	—	
	(1.738)	(1.896)	(2.195)	(119.8)	(113.1)	(107.7)	6.9
$Me_2Ge{=}CH_2$	1.789	1.964	—	122.6	114.8	—	
	(1.799)	(1.967)	(2.650)	(121.7)	(114.2)	(103.9)	3.9
$Me_2Sn{=}CH_2$	1.999	2.177	—	123.1	113.9	—	
	(2.026)	(2.187)	(2.568)	(124.0)	(111.8)	(95.9)	7.5

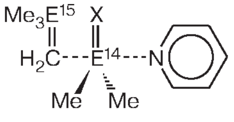
retro-Wittig decomposition of betaines of the first group was examined in pyridine. The geometric parameters of the $Me_2E^{14}{=}X$ compounds and their complexes with pyridine along with the energies of complex formation are given in Table 13.

The formation of complexes with pyridine leads to substantial changes in geometry of the $Me_2E^{14}{=}X$ molecules. The $E^{14}{=}X$ and E^{14}—C bond lengths are increased by 0.3—0.4 Å and ~0.2 Å, respectively. The configuration of the E^{14} atoms becomes pyramidal. It should be noted that the X—E^{14}—N angle in the complexes decreases in the series E^{14} = Si, Ge, and Sn from 103.8—107.7° for Si to 92.5—101.1° for Sn, the more electronegative being the X atom the smaller is the X—E^{14}—N bond angle. This dependence results from the fact that an increase in the atomic number of the E^{14} atom leads to an increase in the contribution of its np_z orbital to LUMO of the $Me_2E^{14}{=}X$ molecule, which is involved in the interaction with the lone electron pair of the nitrogen atom of the pyridine molecule.

As can be seen from the above-considered data, high energies of complex formation not only sharply reduce the endothermic effect of the retro-Wittig decomposition but also principally change the reaction mechanism. As was demonstrated using betaines $^{(-)}X{-}E^{14}Me_2{-}CH_2{-}E^{15(+)}Me_3$ (X = S or Se; E^{15} = Si; E^{15} = P or As) as an example, the reaction proceeds as the bimolecular nucleophilic substitution at the E^{14} atom. For these betaines, the **TS$_b$-pyr** transition states containing the five-coordinate silicon atom and the nearby shallow local minima corresponding to the **C$_b$** complexes can be localized in the reaction coordinate.



TS$_b$-pyr



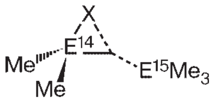
C$_b$

X = S, Se; E^{14} = Si; E^{15} = P, As.

The thermal effect of retro-Wittig-type decomposition of betaine $^{-}S—SiMe_2—CMe_2—P^{+}Ph_3$ (**16a**) in pyridine, which we have observed experimentally (see Section 5), is substantially smaller than that for the corresponding model betaine $^{-}S—SiMe_2—CMe_2—P^{+}Me_3$. According to the results of calculations without considering and taking into account cyclodimerization of $S=SiMe_2$, the thermal effect is 30.9 and −3.1 kcal mol^{-1}, respectively. The calculated values are in satisfactory agreement with the experimental results.

6.2.5. Corey—Chaykovsky-type decomposition of betaines I (path c)

Corey—Chaykovsky-type decomposition of betaines of type **I** (path *c*) proceeds as the intramolecular S_{Ni} substitution at the heteroatom resulting in elimination of phosphine (arsine) $E^{15}Me_3$ through the $\mathbf{TS}_c$ transition states. The energies of the $\mathbf{TS}_c$ transition states and the thermal effects of the reaction are given in Table 12. In the initial region of the reaction coordinate, the *cis-gauche* conformation of betaines is transformed into the *anti-trans* conformation. As mentioned in Section 6.2.1, an increase in polarity of the solvent promotes this transformation and facilitates an increase in the occupancy of the *anti-trans* conformation. However, more precise estimates of the effect of the solvent on the reaction rate can be obtained only within the framework of more sophisticated models because the polarities of the $\mathbf{TS}_c$ transition states (μ ~ 7 D) are lower than those of betaines adopting an *anti-trans* conformation. The heterocyclopropanes formed as the products are highly reactive and undergo exothermic dimerization (see Table 12).

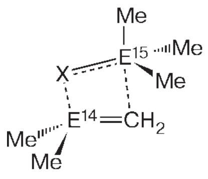


$\mathbf{TS}_c$

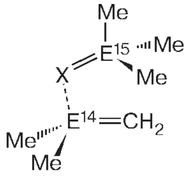
The activation energy of this process increases in the series Si < Ge < Sn except for X = NMe. On going from phosphorus-containing betaines to arsenic-containing analogs, the activation energies decrease by 5—15 kcal mol^{-1} with a simultaneous increase in stability of the reaction products.

6.2.6. Wittig-type decomposition of betaines I (path d)

Wittig-type decomposition of betaines to form ylides $X=E^{15}Me_3$ (X = S, Se, O, or NMe; E^{15} = P or As) and compounds $Me_2E^{14}=CH_2$ (E^{14} = Si, Ge, or Sn) proceeds through the four-membered $\mathbf{TS}_d$ states. The reaction coordinates for decomposition of betaines have pronounced local minima corresponding to post-reaction complexes $\mathbf{C}_d$ in which the leaving $X=E^{15}Me_3$ molecules remain coordinated to the positively charged E^{14} atoms through the X atoms.



$\mathbf{TS}_d$



$\mathbf{C}_d$

Compounds $Me_2E^{14}=CH_2$ can undergo further exothermic cyclodimerization to produce diheteracyclobutanes $(Me_2E^{14}CH_2)_2$. The activation barriers and thermal effects of the reactions are given in Table 12. The $\mathbf{TS}_d$ transition states are less polar (μ ~ 4 D) than the transition states generated in the Corey—Chaykovsky decomposition.

Compounds with the $E^{14}=C$ double bonds are highly polar and form complexes with pyridine. The calculated gain in the energy is in the range of 3.9—7.5 kcal mol^{-1}. The formation of such complexes leads to additional stabilization of the products of their decomposition through the Wittig-type reaction.

According to the results of calculations, the activation barrier to Corey—Chaykovsky-type decomposition for silicon-containing betaines of the first group possessing the thiolate center is 5 kcal mol^{-1} lower than the barrier to Wittig-type decomposition. Correspondingly, photolysis and thermolysis of these betaines lead only to elimination of phosphine or arsine (see Section 5). However, the reverse ratio was observed for germanium- and tin-containing betaines. In these cases, Wittig decomposition must be prevailing because this process is favored also by the thermodynamic factor, *viz.*, by the large total thermal effects of the reaction taking into account cyclodimerization of compounds with the $E^{14}=C$ double bonds.

It should be emphasized that Wittig decomposition of betaines with X = O or NMe, E^{14} = Ge or Sn, and E^{15} = P is the kinetically and thermodynamically most favorable process. In the case of $Me_3P^{(+)}—CH_2—GeMe_2—O^{(-)}$ betaine, the activation energy of formation of germene $Me_2Ge=CH_2$ is only 5.5 kcal mol^{-1}. These conclusions call for experimental verification.

6.3. Structures and potential energy surfaces of betaines II $^{(+)}Me_3E^{15}—CH_2—E^{14}Me_2{}^{(-)}$ (E^{14} = Si, Ge, Sn; E^{15} = P, As)

We investigated the structures and potential energy surfaces of betaines **II** using the model $^{(+)}Me_3E^{15}—CH_2—E^{14}Me_2{}^{(-)}$ compounds (E^{14} = Si, Ge, or Sn; E^{15} = P or As).**116** The principal calculated geometric parameters of these betaines are given in Table 14. In these compounds, the $E^{14}—C$ bonds in the $E^{14}—C—E^{15}$ fragment are substantially longer than the $E^{14}—Me$ bonds. This difference is particularly pronounced for tin-containing betaines. The $E^{14}—C—E^{15}$ bond angles are somewhat smaller than the ideal tetrahedral value (109.5°). These effects result from the fact that the Coulomb at-

Table 14. Principal geometric parameters of betaines $^{(+)}Me_3E^{15}—CH_2—E^{14}Me_2^{(-)}$ (E^{14} = Si, Ge, or Sn; E^{15} = P or As) (interatomic distances (*d*) and bond angles (φ))

Betaine	*d*/Å				φ/deg
	E^{14}—C	$E^{14}—C_{Me}$	C—E	$E^{14}...E^{15}$	E^{14}—C—E^{15}
P—C—Si	2.057	1.952	1.777	3.103	107.8
P—C—Ge	2.192	2.045	1.763	3.209	107.9
P—C—Sn	2.410	2.248	1.756	3.445	110.6
As—C—Si	2.034	1.950	1.911	3.122	104.6
As—C—Ge	2.168	2.044	1.896	3.237	105.4
As—C—Sn	2.390	2.248	1.887	3.484	108.5

traction between the anionic $E^{14}Me_2^{(-)}$ center and the cationic $^{(+)}E^{15}Me_3$ center competes with the 1,3-repulsion between the terminal groups. The interatomic $E^{14}...E^{15}$ distances in betaines are approximately 0.8 Å smaller than the sums of the corresponding van der Waals radii (see Table 14).

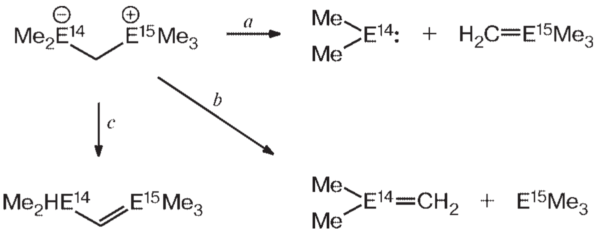
Three main pathways of chemical transformation of betaines **II** were examined (Scheme 38).

1. Decomposition with elimination of arsenic or phosphorus ylide to produce Me_2E^{14} (silylene, germylene, or stannylene), which is the reverse of the synthesis of these betaines.

2. Decomposition to give compounds $Me_2E^{14}=CH_2$ and phosphine (arsine) $E^{15}Me_3$.

3. Isomerization into metallated ylides $Me_2HE^{14}—CH=E^{15}Me_3$.

Scheme 38



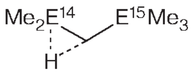
The formation of betaines in the gas-phase reactions of Me_2E^{14} (E^{14} = Si, Ge, or Sn) with ylides $H_2C=E^{15}Me_3$ (E^{15} = P or As) is a barrierless highly exothermic process. The thermal effects of the reactions are given in Table 15.

Elimination of phosphine (arsine) $E^{15}Me_3$ proceeds through the **TS-1** transition state. The activation barriers of this process for organophosphorus betaines are higher than those for organoarsenic betaines. These barriers are increased and the thermal effect of the reaction is reduced in the series E^{14} = Si, Ge, Sn (see Table 15). This type of decomposition is thermodynamically favorable for betaines $Me_2E^{14(-)}—CH_2—AsMe_3^{(+)}$ (E^{14} = Si or Ge), and the global minima on PES correspond to the formation of $Me_2E^{14}=CH_2$ (E^{14} = Si or Ge).

Table 15. Heats of reactions (ΔE^0) and activation energies (E_a/kcal mol^{-1}) for the major pathways of decomposition of betaines $^{(+)}Me_3E^{15}—CH_2—E^{14}Me_2^{(-)}$ (E^{14} = Si, Ge, or Sn; E^{15} = P or As)

Betaine	Reaction *a* ΔE^0	Reaction *b*		Reaction *c*	
		E_a	ΔE^0	E_a	ΔE^0
P—C—Si	35.0	19.3	−5.8	31.5	−22.3
P—C—Ge	30.4	28.2	8.0	40.5	−4.6
P—C—Sn	29.4	36.9	24.4	46.8	7.0
As—C—Si	38.4	8.1	−20.5	34.5	−18.5
As—C—Ge	33.0	15.1	−7.5	41.6	−1.6
As—C—Sn	31.5	22.5	8.4	48.4	9.4

TS-1



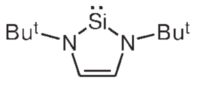
TS-2

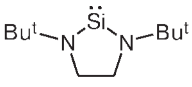
E^{14} = Si, Ge, Sn; E^{15} = P, As.

For betaines $Me_2E^{14(-)}—CH_2—PMe_3^{(+)}$ (E^{14} = Si or Ge), this decomposition is also kinetically most favorable. However, isomerization into ylides $Me_2HE^{14}—CH=PMe_3$ (E^{14} = Si or Ge) leads to the global minima on PES of these compounds. Intramolecular isomerization proceeds through the **TS-2** transition states because it is necessary to overcome high activation barriers (31.5—48.4 kcal mol^{-1}, see Table 15). In this connection, the intermolecular pathway of isomerization may be kinetically more favorable. In polar media, the donor solvent molecule can serve as a proton carrier. All three pathways of the chemical transformations are endothermic for betaines $^{(+)}Me_3E^{15}—CH_2—SnMe_2^{(-)}$ to which the global minima on PES correspond.

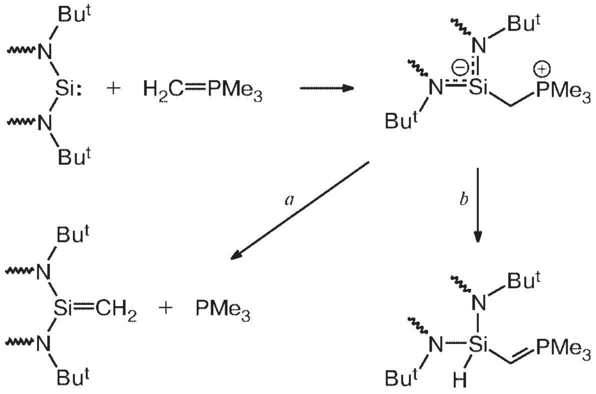
Table 15 gives the thermodynamic data calculated at T = 0 K. It should be noted that the entropy factor is favorable for decomposition of betaines through the paths *a* and *b* at higher temperatures. The reactions of heavier analogs of carbenes with phosphorus and arsenic ylides are poorly studied. The above-considered results of calculations lead to an optimistic prediction that a new procedure for the preparation of heavier $R_2E^{14}=CH_2$ (E^{14} = Si, Ge, or Sn) can be developed based on these reactions.

We carried out theoretical investigation of the reactions of stable West silylenes **28** and **72** with phosphorus ylide $H_2C=PMe_3$. Like the simplest analogs of carbenes, these compounds can form betaines in which the negative and positive charges are located on the silicon and phosphorus atoms, respectively. These betaines can either undergo thermal decomposition to give silenes (Scheme 39, path *a*) or be isomerized into ylides (path *b*).


28

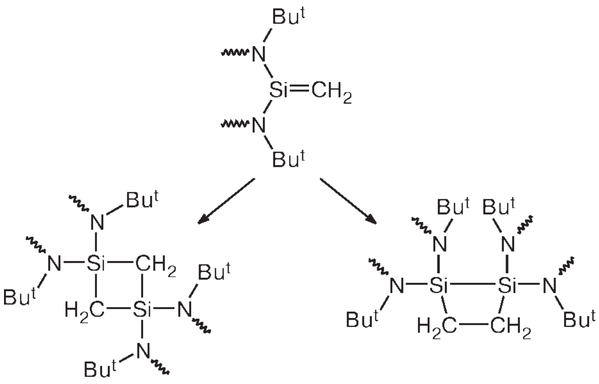

72

Scheme 39



Silenes generated through the path *a* can undergo exothermic dimerization to give two types of dimers (head-to-tail and head-to-head), which differ in thermal stability (Scheme 40). The energy parameters of these reactions are given in Table 16.

Scheme 40


Head-to-tail dimer Head-to-head dimer

Based on analysis of the data presented in Table 16, it can be concluded that the formation of silenes is the kinetically most favorable process. However, according to the experimental data, metallated ylides are generated in these reactions. This result is accounted for by the fact that in polar solvents the proton transfer from the carbon atom to the silicon atom occurs according to an intermolecular mechanism, which leads to a substantial decrease in the barrier to the reaction. We believe that elimination of phosphines giving rise to silenes can be the most probable process if the migration of substituents from carbon to silicon will be suppressed, for example, by introducing two alkyl radicals.

Table 16. Energies of stationary points on PES (E^0/kcal mol^{-1}) for the reactions of West's silylenes **28** and **72** with $H_2C=PMe_3$

Stationary points	E^0/kcal mol^{-1}	
	28	**72**
Silylene + $H_2C=PMe_3$	0.0	0.0
Betaine	−2.9	−6.8
TS$_a$	8.5	2.9
Silylene + PMe_3	−1.0	−9.0
1/2 H—T—H dimer + PMe_3	−29.3	−39.2
1/2 H—T—H dimer + PMe_3	−21.5	−30.5
TS$_b$	35.6	29.3
Ylide	−18.4	−26.1

7. Conclusion

The data on the structures and reactivities of heteroorganic betaines **I** and **II** presented in this review demonstrate that these compounds lie at a "lively intersection of chemical roads," which open up new attractive possibilities for performing interconversions of heavy analogs of carbenes (silylenes, germylenes, and stannylenes), on the one hand, and compounds containing the $E^{14}=X$ multiple bonds or small rings involving Group 14 elements, on the other hand. In the last decades, the chemistry of these compounds has been developed very extensively. It is evident that the above-mentioned compounds must be considered in common because their structures and properties are to a large extent determined by the same factors, general approaches are employed in their syntheses and investigations, and a series of chemical reactions are known in which these compounds undergo interconversions. The chemistry of betaines of types **I** and **II** is still in its infancy. However, it is already apparent that these compounds can be involved in a broad range of reactions. The results of theoretical analysis lead to an optimistic prediction that these reactions can provide the basis for the development of new general procedures for the preparation of heteroalkenes $R_2E^{14}=CH_2$ (E^{14} = Si, Ge, or Sn) or their generation as short-lived intermediates.

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References

1. R. Tacke, M. Pulm, and B. Wagner, *Adv. Organomet. Chem.*, 1999, **44**, 221.
2. S. Venne-Dunker, W. Ahlers, G. Erker, and R. Fröhlich, *Eur. J. Inorg. Chem.*, 2000, 1671.
3. R. Chauvin, *Eur. J. Inorg. Chem.*, 2000, 577.
4. B. Alcaide, L. Cassarrubios, G. Deminguer, and M. A. Sierra, *Curr. Org. Chem.*, 1998, **2**, 551.
5. A. W. Johnson, *Ylides and Imines of Phosphorus*, Wiley Int., New York, 1993.
6. O. I. Kolodiazhnyi, *Phosphorus Ylides. Chemistry and Application in Organic Synthesis*, Wiley-VCH, Weinheim—New York—Chichester, 1999.
7. E. Vedejs and M. J. Peterson, in *Advances in Carbanion Chemistry*, Ed. V. Sniekus, JAI Press, Greenwich (CT), 1996, **2**, 1.
8. E. Vedejs and M. J. Peterson, *Top. Stereochem.*, 1994, **21**, 1.
9. E. Vedejs and C. F. Marth, in *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*, Eds. L. D. Quin and J. G. Verkade, VCH, New York, 1994, 297.
10. C. Geletneky, F. H. Fersterling, W. Bock, and S. Berger, *Chem. Ber.*, 1993, **126**, 2397.
11. R. A. Neumann and S. Berger, *Eur. J. Org. Chem.*, 1998, 1085.
12. I. V. Borisova, N. N. Zemlyansky, A. K. Shestakova, and Yu. A. Ustynyuk, *Mendeleev Commun.*, 1996, 90.
13. C. Puke, G. Erker, N. C. Aust, E. U. Würthwein, and R. Fröhlich, *J. Am. Chem. Soc.*, 1998, **120**, 4863.
14. C. Puke, G. Erker, B. Wibbeling, and R. Fröhlich, *Eur. J. Org. Chem.*, 1999, 1831.
15. I. V. Borisova, N. N. Zemlyanskii, A. K. Shestakova, and Yu. A. Ustynyuk, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 2140 [*Russ. Chem. Bull.*, 1993, **42**, 2053 (Engl. Transl.)].
16. I. V. Borisova, N. N. Zemlyanskii, Yu. A. Ustynyuk, V. N. Khrustalev, S. V. Lindeman, and Yu. T. Struchkov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 339 [*Russ. Chem. Bull.*, 1994, **43**, 318 (Engl. Transl.)].
17. *Multiply Bonded Main Group Metals and Metalloids*, Eds. R. West and F. G. A. Stone, Academic Press, San Diego, 1996.
18. *Organosilicon Chemistry III. From Molecules to Materials*, Eds. N. Auner and J. Weis, Wiley-VCH, 1998.
19. A. H. Li, L. X. Dai, and V. K. Aggarval, *Chem. Rev.*, 1997, **97**, 2341.
20. A. G. Brook and A. MacMillan, *J. Organomet. Chem.*, 1988, **341**, C9.
21. Yu. A. Ustynyuk, P. I. Zakharov, A. A. Azizov, and G. A. Shchembelov, *J. Organomet. Chem.*, 1975, **96**, 195.
22. Y. Nakadaira, H. Sakaba, and H. Sarurai, *Chem. Lett.*, 1980, 1071.
23. T. G. Barton, G. T. Burns, E. V. Arnold, and J. Clardy, *Tetrahedron Lett.*, 1981, **22**, 287.
24. N. N. Zemlyanskii, I. V. Borisova, Yu. N. Luzikov, N. D. Kolosova, Yu. A. Ustynyuk, and I. P. Beletskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 2668 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1980, **29** (Engl. Transl.)].
25. N. N. Zemlyanskii, I. V. Borisova, Yu. N. Luzikov, Yu. A. Ustynyuk, N. D. Kolosova, and I. P. Beletskaya, *Zh. Org. Khim.*, 1981, **17**, 1323 [*J. Org. Chem. USSR*, 1981, **17** (Engl. Transl.)].
26. N. N. Zemlyanskii, I. V. Borisova, Yu. N. Luzikov, V. K. Belsky, Yu. A. Ustynyuk, and I. P. Beletskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2837 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30** (Engl. Transl.)].
27. V. K. Belsky, N. N. Zemlyanskii, I. V. Borisova, N. D. Kolosova, and I. P. Beletskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1184 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30** (Engl. Transl.)].
28. V. K. Belsky, N. N. Zemlyansky, I. V. Borisova, N. D. Kolosova, and I. P. Beletskaya, *Cryst. Struct. Comm.*, 1982, **11**, 497.
29. V. K. Belsky, N. N. Zemlyansky, I. V. Borisova, N. D. Kolosova, and I. P. Beletskaya, *Cryst. Struct. Comm.*, 1982, **11**, 881.
30. V. L. Yarnykh, V. I. Mstislavskii, N. N. Zemlyanskii, I. V. Borisova,. Yu. A. Roznyatovskii, and Yu. A. Ustynyuk, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1285 [*Russ. Chem. Bull.*, 1997, **46**, 1228 (Engl. Transl.)].
31. P. R. Jones, J. M. Rozell, and B. M. Campbell, *Organometallics*, 1988, **4**, 1321.
32. I. V. Borisova, N. N. Zemlyanskii, Yu. A. Ustynyuk, I. P. Beletskaya, and E. A. Chernyshev, *Metalloorg. Khim.,* 1992, **5**, 548 [*Organomet. Chem. USSR*, 1992, **5** (Engl. Transl.)].
33. I. V Borisova, N. N. Zemlyansky, V. K. Belsky, N. D. Kolosova, A. N. Sobolev, Yu. N. Luzikov, Yu. A. Ustynyuk, and I. P. Beletskaya, *J. Chem. Soc.*, *Chem. Commun.*, 1982, 1090.
34. I. V. Borisova, N. N. Zemlyanskii, Yu. N. Luzikov, Yu. A. Ustynyuk, V. K. Belsky, N. D. Kolosova, M. M. Shtern, and I. P. Beletskaya, *Dokl. Akad. Nauk SSSR,* 1983, **269**, 90 [*Dokl. Chem.*, 1983 (Engl. Transl.)].
35. C. Couret, J. Escudie, J. Satge, and M. Lazraq, *J. Am. Chem. Soc.*, 1987, **109**, 4411.
36. M. Lazraq, J. Escudie, C. Couret, J. Satge, M. Druger, and R. Dammel, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 828.
37. M. Lazraq, C. Couret, J. Escudie, J. Satge, and M. Soufiaoui, *Polyhedron*, 1991, **10**, 1153.
38. M. A. Chaubon, J. Escudie, H. Ranaivonjatovo, and J. Satge, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 893.
39. G. Anselme, C. Couret, J. Escudie, S. Rishelme, and J. Satge, *J. Organomet. Chem.*, 1991, **418**, 321.
40. G. Anselme, H. Ranaivonjatovo, J. Escudie, C. Couret, and J. Satge, *Organometallics*, 1992, **11**, 2748.
41. C. Couret, J. Escudie, G. Delpon-Lacaze, and J. Satge, *J. Organomet. Chem.*, 1992, **440**, 233.
42. I. V. Borisova, N. N. Zemlyansky, A. K. Shestakova, and Yu. A. Ustynyuk, *Mendeleev Commun.*, 1996, 229.
43. N. N. Zemlyanskii, I. V. Borisova, A. K. Shestakova, Yu. A. Ustynyuk, and E. A. Chernyshev, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 486 [*Russ. Chem. Bull.*, 1998, **47**, 469 (Engl. Transl.)].
44. G. Erker, R. Hock, S. Wilker, C. Laurent, R. Puke, E.-U. Wurtheim, and R. Frohlich, *Phosphorus, Sulfur, Silicon Relat. Elem.*, 1999, **153—154**, 79.

45. A. G. Brook and A. M. Brook, *Adv. Organomet. Chem.*, 1996, **39**, 71.
46. I. Hemme and U. Klingebiel, *Adv. Organomet. Chem.*, 1996, **39**, 159.
47. M. Driess, *Adv. Organomet. Chem.*, 1996, **39**, 193.
48. R. Okazaki and R. West, *Adv. Organomet. Chem.*, 1996, **39**, 232.
49. J. Escudie and H. Ranaivonjatovo, *Adv. Organomet. Chem.*, 1999, **44**, 113.
50. I. V. Borisova, N. N. Zemlyanskii, A. K. Shestakova, Yu. A. Ustynyuk, and E. A. Chernyshev, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 2143 [*Russ. Chem. Bull.*, 1993, **42**, 2056 (Engl. Transl.)].
51. I. V. Borisova, N. N. Zemlyanskii, A. K. Shestakova, Yu. A. Ustynyuk, and E. A. Chernyshev, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 922 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 920].
52. I. V. Borisova, N. N. Zemlyanskii, M. G. Kuznetsova, V. N. Khrustalev, M. S. Nechaev, and Yu. A. Ustynyuk, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 1601 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 1679].
53. Yu. A. Ustynyuk, M. S. Nechaev, D. N. Laikov, I. V. Borisova, N. N. Zemlyanskii, V. N. Khrustalev, M. G. Kuznetsova, and A. K. Shestakova, *Abstrs. of Papers, Int. Conf. "Lomonosov Readings 2001,"* Moscow, 2001, 6.
54. K. A. Kocheshkov, N. N. Zemlyanskii, N. I. Sheverdina, and E. M. Panov, *Metody elementoorganicheskoi khimii. Germanii. Olovo. Svinets* [*Methods of Organoelement Chemistry. Germanium. Tin. Lead*], Nauka, Moscow, 1968, 105 pp. (in Russian).
55. D. Lloyd, I. Gosney, and R. A. Ormiston, *Chem. Soc. Rev.*, 1987, **16**, 45.
56. D. Lloyd and I. Gosney, in *The Chemistry of Organic Arsenic, Antimony, and Bismuth Compounds*, Ed. S. Patai, Wiley Chichester, 1994.
57. I. V. Borisova, N. N. Zemlyanskii, M. G. Kuznetsova, V. N. Khrustalev, M. S. Nechaev, and Yu. A. Ustynyuk, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 627 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, No. 4].
58. R. Oda, Y. Ito, and M. Okano, *Tetrahedron Lett.*, 1964, 7.
59. Y. Ito, M. Okano, and R. Oda, *Tetrahedron*, 1966, **22**, 2615.
60. G. A. Wheaton and N. J. Burton, *Tetrahedron Lett.*, 1976, 895.
61. M. Veith and V. Huch, *J. Organomet. Chem.*, 1985, **293**, 161.
62. M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner, and N. Metzler, *J. Am. Chem. Soc.*, 1994, **116**, 2691.
63. V. N. Khrustalev, I. V. Borisova, N. N. Zemlyanskii, and Yu. A. Ustynyuk, and M. Yu. Antipin, *Kristallografiya*, 2002, No. 4 [*Crystallogr. Repts.*, 2002, No. 4 (Engl. Transl.)].
64. J. Barrau, G. Rima, and T. El Amraoui, *Organometallics*, 1998, **17**, 607.
65. M. S. Nechaev and Yu. A. Ustynyuk, in *Abstrs. of Papers, X Int. Conf. on Coordination and Organometallic Chemistry of Germanium, Tin, and Lead*, Bordeaux, France, June 7—12, 1P61.
66. N. N. Zemlyansky, I. V Borisova, M. G. Kuznetsova, V. N. Khrustalev, M. S. Nechaev, J. Barrau, G. Rima, and Yu. A. Ustynyuk, *Organometallics*, 2002.
67. H. Grützmacher, W. Deck, H. Pritzkow, and M. Sander, *Angew. Chem.*, 1994, 106; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 456.
68. V. N. Khrustalev, N. N. Zemlyanskii, I. V. Borisova, Yu. A. Ustynyuk, and E. A. Chernyshev, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 933 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 929].
69. A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
70. F. H. Allen, O. Kennard, D. G. Watson, A. G. Orpen, L. Brammer, and R. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, 1987, S1.
71. H. Suzuki, N. Tokitoh, S. Nagase, and R. Okazaki, *J. Am. Chem. Soc.*, 1994, **116**, 11578.
72. *Cambridge Crystal Structure Database*, Cambridge, Release 2000.
73. M. Veith and V. Huch, *J. Organomet. Chem.*, 1986, **308**, 263.
74. K.-H. Dreihäupt, K. Angermaier J. Riede, and H. Schmidbaur, *Chem. Ber.*, 1994, **127**, 1599.
75. H. Schmidbaur, R. Pichl, and G. Muller, *Chem. Ber.*, 1987, **120**, 789.
76. I. V. Borisova, N. N. Zemlyanskii, A. K. Shestakova, V. N. Khrustalev, Yu. A. Ustynyuk, and E. A. Chernyshev, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 935 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 933].
77. T. A. Albright, W. J. Freeman, and E. E. Schweizer, *J. Am. Chem. Soc.*, 1975, **97**, 2542.
78. T. A. Albright, M. Gordon, W. J. Freeman, and E. E. Schweizer, *J. Am. Chem. Soc.*, 1976, **98**, 6249.
79. T. Kawashima, T. Iijima, H. Kikuchi, and R. Okazaki, *Phosphorus, Sulfur, Silicon*, 1999, **144—146**, 149.
80. I. V. Borisova, Ph. D. (Chem.) Thesis, M. V. Lomonosov Moscow State University, Moscow, 1983 (in Russian).
81. H. Schmidbaur and W. Tronich, *Chem. Ber.*, 1968, **101**, 595.
82. S. Wilker, C. Laurent, C. Sarter, C. Puke, and G. Erker, *J. Am. Chem. Soc.*, 1995, **117**, 7293.
83. B. E. Maryanoff and A. B. Reitz, *Chem. Rev.*, 1989, **89**, 863.
84. I. V. Borisova, N. N. Zemlyanskii, A. K. Shestakova, V. N. Khrustalev, Yu. A. Ustynyuk, and E. A. Chernyshev, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 1594 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 1583].
85. T. Tsumuraya, S. Sato, and W. Ando, *Organometallics*, 1989, **8**, 161.
86. P. Jutzi and A. Mohrke, *Angew. Chem.*, *Int. Ed. Engl.*, 1989, **28**, 762.
87. J. Barrau, G. Rima, M. El Amin, and J. Satge, *J. Organomet. Chem.*, 1988, **345**, 39.
88. J. Barrau, G. Rima, and J. Satge, *J. Organomet. Chem.*, 1983, **252**, C73.
89. Yu. L. Slovokhotov, T. V. Timofeeva, M. Yu. Antipin, and Yu. T. Struchkov, *J. Mol. Struct.*, 1984, **112**, 127.
90. A. S. Batsanov, M. G. Davidson, J. A. K. Howard, S. Lamb, and C. Lustig, *Chem. Commun.*, 1996, 1791.
91. G. A. Gornowicz and R. West, *J. Am. Chem. Soc.*, 1968, **90**, 4478.
92. D. J. Peterson, *J. Organomet. Chem.*, 1967, **9**, 373.
93. I. V. Borisova, N. N. Zemlyanskii, A. K. Shestakova, V. N. Khrustalev, Yu. A. Ustynyuk, and E. A. Chernyshev, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 935 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 933].

94. I. V. Borisova, N. N. Zemlyansky, A. K. Shestakova, V. N. Khrustalev, and Yu. A. Ustynyuk, *Mendeleev Commun.*, 1997, 10.
95. S. Scheithauer and R. Mayer, *Chem. Ber.*, 1967, **100**, 1413.
96. H. Schmidbaur, *Acc. Chem. Res.*, 1975, **8**, 62.
97. N. N. Zemlyanskii, I. V. Borisova, A. K. Shestakova, Yu. A. Ustynyuk, and E. A. Chernyshev, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 2246 [*Russ. Chem. Bull.*, 1994, **43**, 2126 (Engl. Transl.)].
98. M. G. Voronkov and S. V. Basenko, *J. Organomet. Chem.*, 1995, **500**, 325.
99. J. Kapp, M. Remko, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1996, **118**, 5745.
100. H. Schmidbaur and W. Tronich, *Chem. Ber.*, 1967, **100**, 1023.
101. K. A. O. Starzewski and H. T. Dieck, *Phosphorus*, 1976, **6**, 177.
102. E. Schaumann and F.-F. Grabley, *Liebigs Ann. Chem.*, 1979, 1702.
103. J. Bestmann, R. Engler, H. Hartung, and K. Roth, *Chem. Ber.*, 1979, **112**, 28.
104. H. Schmidbaur, J. Eberlein, and W. Richter, *Chem. Ber.*, 1977, **110**, 677.
105. H. Schmidbaur, H. Stuhler, and W. Buchner, *Chem. Ber.*, 1973, **106**, 1238.
106. D. Seyferth, D. P. Duncan, H. Schmidbaur, and P. Holl, *J. Organomet. Chem.*, 1978, **159**, 137.
107. H. Schmidbaur and W. Wolf, *Chem. Ber.*, 1975, **108**, 2834.
108. H. Schmidbaur, W. Richter, W. Wolf, and F. H. Kohler, *Chem. Ber.*, 1975, **108**, 2642.
109. H. Gilman and R. A. Tomasi, *J. Org. Chem.*, 1962, **27**, 3647.
110. *Encyclopedia of Computational Chemistry*, Eds. P. v. R. Schleyer, N. L. Allinger, T. Clark, P. A. Kollman, H. F. Schafer III, and P. R. Scheiner, Wiley-VCH, Chichester, 1998, **1—5**.
111. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
112. D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.
113. D. N. Laikov, Ph. D. (Phys.-Mat.) Thesis, M. V. Lomonosov Moscow State University, Moscow, 2000 (in Russian).
114. M. S. Nechaev, I. V. Borisova, N. N. Zemlyanskii, D. N. Laikov, and Yu. A. Ustynyuk, *Izv. Akad. Nauk, Ser. Khim.*, 2000 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 1823,].
115. M. S. Nechaev, I. V. Borisova, N. N. Zemlyansky, D. N. Laikov, and Yu. A. Ustynyuk, *2nd V. A. Fock School (Conference) on Quantum and Computational Chemistry, (Novgorod, January 31—February 4, 2000), Book of Abstrs.*, p. 43, 44.
116. M. S. Nechaev, I. V. Borisova, N. N. Zemlyansky, D. N. Laikov, and Yu. A. Ustynyuk, *3rd V. A. Fock Conference for Quantum and Computational Chemistry (Novgorod, May 21—22, 2001), Book of Abstrs.*, p. 100.

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